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OF THE

INDIAN ACADEMY OF SCIENCES

VOL. XXXII] *SECTION A* [No. 1

JULY, 1950

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO,
SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES,
BANGALORE.

THE STRUCTURE OF LABRADORITE AND THE ORIGIN OF ITS IRIDESCENCE

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Received July 14, 1950

1. Introduction

Labradorite which is a crystalline feldspar of the triclinic class is well known for the striking iridescence or play of colours which it exhibits. The phenomenon is displayed not only by specimens from the locality which gave its name to the substance, namely the coast of Labrador, but also by those from other parts of the world. This fact and the highly distinctive character of the effects observed suggest that they are in some way connected with the nature of the feldspar itself. Hintze (1897) reviewed the earlier attempts to find an explanation of the iridescence. Later investigations published about the same time by Rayleigh (1923) and by Boggild (1924) made useful contributions to the subject; but they left unanswered the fundamental questions which arise, namely, what is the material which is responsible for the iridescence of labradorite and why is it present? In the hope that a more searching examination of the phenomena than has hitherto been made might result in finding the answers to these questions, a representative collection of specimens was acquired for the crystallographic museum of this Institute. They have been carefully studied, and the investigation has revealed basic new facts concerning the iridescence of labradorite and enabled us to reach definite conclusions regarding its origin.

2 The Chemical Composition of Labradorite

Mineralogists place labradorite fairly high up in the sequence of the plagioclase feldspars running from albite to anorthite. The two end-members of the series both belong to the triclinic class of crystals, and it is a well-established fact that they are isomorphous and can mix freely in all proportions to form homogeneous crystals. To describe labradorite as a mixture of albite and anorthite, in other words of soda and lime feldspars is, however, only an idealisation and not a complete picture of the reality. The chemical analyses tabulated by Hintze (*loc. cit.*) show that labradorite contains also an appreciable proportion of potash feldspar. There are also other materials present as impurities in variable amounts, these being principally Fe_2O_3 and MgO. Examination of labradorite under a binocular microscope shows the

presence of inclusions of different kinds trapped at various levels within the crystal. They appear as discrete crystals with sharply defined outlines and evidently represent the impurities revealed by the chemical analysis. Their distribution within the labradorite is irregular, even in those cases in which the characteristic iridescence of the feldspar appears with remarkably uniform intensity and colour over the entire volume of the specimen. The facts stated make it highly improbable that the characteristic iridescence of labradorite is due to the presence in it of extraneous impurities or inclusions. They suggest, rather, that the phenomenon has its origin in the constitution of the feldspar itself. Our attention is thus naturally directed to the third component of the feldspar shown by the chemical analysis to be present, namely, orthoclase or potash feldspar.

3. The Lamellar Structure of the Mixed Feldspars

The crystallographic data and the X-ray investigations that have been made (Taylor, 1934) indicate that all the feldspars possess certain structural features in common. Nevertheless, there are well-established differences amongst them, the most notable being that the feldspars in which the potash is the principal component crystallise in the monoclinic system, whereas those in which the soda and lime feldspars are the principal components form triclinic crystals. In view of its lack of isomorphism with the two other feldspars, we could scarcely expect potash feldspar to be freely miscible with them in all proportions or to form homogeneous crystals as the result of such mixture. Actually, when the results of the chemical analyses of nearly a thousand specimens of naturally occurring feldspars are plotted as points on a three-component diagram (Alling, 1921), it is found that a large part of the area of the triangle is empty and that a potash-lime series of feldspars is not represented in the diagram. The occupied area consists of a belt lying along the two sides of the triangle representing respectively a soda-potash series of feldspars and a soda-lime series, its width being greatest in the vicinity of the vertex representing pure albite and narrowing rapidly as the vertices representing pure orthoclase and pure anorthite are approached. It should be emphasised that the feldspars found in nature are not invariably homogeneous crystals. Indeed, it is well known that many of the feldspars of the soda-potash series are not of that description. Amongst the feldspars of the series in which orthoclase is the major component, only those containing a relatively small proportion of albite are truly single crystals. The others are essentially intergrowths in which the monoclinic and triclinic components have separated from each other to form lamellar structures. The lamellæ may be so coarse as to be visible to the naked eye (perthites);

they may also be so fine as to be visible only under a microscope or even so fine as to be optically irresolvable (microperthites).

In view of what has been said above, the question arises as to how the component of potash feldspar present in the soda-lime series of feldspars is distributed within the material, *viz.*, whether it forms a homogeneous solid solution with the albite-anorthite, or whether it is segregated from the soda-lime feldspar and forms crystallites of orthoclase which remain embedded in the albite-anorthite matrix and distributed through its volume. The latter alternative has to be recognised at least as a possibility. The optical behaviour of labradorite would be profoundly different according as the first or the second alternative is the correct answer. In the former case, it would be a transparent colourless crystal, assuming that there are no other inclusions or impurities present. In the second case, the difference in refractivity between the orthoclase crystallites and the albite-anorthite mass in which they are embedded is considerable. Hence their presence would render the crystal an optically heterogeneous medium, causing it to exhibit various effects when traversed by a beam of light. Since labradorite does exhibit such effects, we are entitled, at least as a working hypothesis, to adopt the second of the alternatives stated and to develop its consequences for comparison with the facts of observation.

4. The Orientation of the Lamellæ

Accepting the validity of our hypothesis, we have to ask ourselves other questions, *viz.*, what is the shape, size and orientation of the crystallites of orthoclase? Is the setting of the crystallites arbitrary and unrelated to the structure of the albite-anorthite crystal, or does it have some definite relation to it and therefore possesses some measure of uniformity?

In seeking an answer to the questions raised, the facts which have been established by X-ray investigations on the soda-potash series of feldspars give us some useful guidance. Ito and Inuzuke (1936) found that two structures are present in the microperthites, one similar to pure potash-orthoclase, the other similar to albite. Their work has been confirmed by Chao, Smare and Taylor (1939), while a further study by Chao and Taylor (1940) revealed some finer details. For our present purpose, the principal result that emerges from the X-ray studies is that the crystal axes of the two structures present in the microperthites are either coincident, or else make small angles with each other. The latter result is not unexpected, since one of the structures is monoclinic and the other triclinic. We have, therefore, ample justification for assuming that a similar situation would exist in our present problem, in other words, that the crystal structures of the orthoclase and of the

surrounding albite-anorthite mass would be coherent. From a crystallographic point of view, therefore, we may, without serious error, consider the whole of the material as a single unit in spite of its optical heterogeneity.

In the circumstances stated, it is not unreasonable to assume that the actual shape and setting of the orthoclase crystallites would bear some recognisable relationship to the lattice structure of the enclosing crystalline mass. According to Chao and Taylor (1940), the crystal structure of labradorite is itself rather complex, sheets of albite and sheets of anorthite, each a few unit cells thick, alternating along the *c*-axis. In these circumstances, it is scarcely possible even to venture a guess as how the third component, *viz.*, the monoclinic orthoclase would dispose of itself in the lattice. We have necessarily to regard this as a matter for observational study rather than for theoretical prediction. Nevertheless, as will be shown in the following sections of the paper, the theoretical ideas set out above have various specific consequences which can be tested by observation or experiment. The complete success met with in such tests is testimony to their essential correctness.

5. Some Consequences of the Twinning of Labradorite

As is well known, the plagioclase feldspars frequently exhibit multiple or repeated twinning of the albite type. The brachypinacoid or 010 face is both a plane of reflection and a plane of composition in this type of twinning; in other words, the crystal structures on either side of a composition plane are mirror images of each other. The albite type of twinning is readily recognized by the appearance of sets of parallel lines where the composition planes meet the external surface of the crystal. They are most clearly seen on the 001 faces, since these are the most perfect cleavages of the crystal and are nearly normal to the twinning planes. The visible signs of albite twinning on the 001 faces may be traced across them right up to the edges of any artificially polished surface which meets them. We shall proceed to consider how such twinning would influence the optical phenomena exhibited by labradorite.

It will be assumed that the iridescence displayed by labradorite arises from the presence in it of thin lamellæ of orthoclase which reflect a beam of light travelling through the crystal by virtue of their refractive index being less than that of the surrounding albite-anorthite mass. The direction in which the light is reflected would depend on the angle of its incidence on the lamellæ and hence also on the orientation of the latter within the crystal. This orientation is more or less precisely defined, being determined by physico-chemical considerations connected with the crystal structures of the three components of the feldspar. Further, the orthoclase lamellæ, though

optically different from the surrounding mass, are nevertheless an integral part of the crystal. Hence, if the latter is a simple albite twin, the orientations of the lamellæ in the components of the twin would not be identical but would be mirror-images of each other with respect to their composition plane. For the same reason, also, if the labradorite is a multiple or repeated twin, the orientations of the lamellæ in the 1st, 3rd, 5th, etc. twinning layers of the crystal would be parallel to each other, and likewise also the orientation of the lamellæ in the 2nd, 4th, 6th, etc. twinning layers, but the orientations of the lamellæ in the two sets of twinning layers would be different, being the mirror images of each other in the composition planes. The *thickness* of the orthoclase lamellæ influences their optical behaviour, including especially the colour which they exhibit. If this be the same in the 1st, 3rd, 5th, etc. twinning layers of the crystal, there is no reason why it should be different in the intervening 2nd, 4th, 6th, etc. layers. Hence, we arrive at the following inferences as necessary consequences of our theoretical views.

A. *Every specimen of labradorite which is twinned according to the albite law and exhibits iridescence, should display the latter in two distinct settings of the specimen, if the direction of incidence of the light and the direction of observation are pre-determined.*

B. *For the same reason, for any given setting of the specimen and a given direction of incidence of the light on it, the iridescence should be observable in two divergent directions.*

C. *The two reflections mentioned above have their origin in different parts of the crystal, namely the two differently orientated sets of components of the multiple twin.*

D. *The two sets of reflections should in similar circumstances exhibit identical colours.*

E. *The settings of the crystal required for observing the two independent sets of reflections should make equal angles with the setting required to obtain a specular reflection from the composition planes of the twinning.*

Another kind of twinning which is frequently observed in the plagioclase feldspars is known as the pericline type. This species of twinning is almost invariably multiple with closely spaced components, the structures of which are derivable from each other by a rotation of the crystal about the *b*-axis through 180°. The composition planes of the pericline twinning in labradorite are nearly parallel to the 001 faces of the crystal, actually making an angle only 6° with them. The twinning manifests itself externally by parallel

and closely spaced striations on the 010 faces of the crystal and is thus readily distinguishable from the albite twinning where no such striations are observed.

Reasoning analogous to that set out in the case of albite twinning leads to theoretical consequences similar to those listed above as A, B, C, D and E, except that the word "pericline" is substituted for "albite" in the description of the twinning and E is modified to read as follows:—

E'. *The settings of the crystal required for observing the two independent sets of reflections would be obtained, one from the other, by a rotation of the crystal about its* b*-axis through* 180°.

6. Comparison with the Facts of Observation

Our theory thus leads us to the remarkable conclusion that precisely definable relationships should exist between the kind of twinning of the albite or the pericline type, as the case may be, which a particular specimen of labradorite exhibits and the circumstances in which it displays iridescence as well as the observable characters of such iridescence. It is scarcely conceivable that any such relationships could exist unless it is the case that the material responsible for the iridescence of the feldspar is itself an integral part of the structure of the crystal. It follows that relationships indicated by the theory, if they actually exist, are a convincing demonstration of its correctness.

The specimens of labradorite at our disposal form a fairly representative collection, both in regard to the colours exhibited and in respect of their types of twinning as identified by their external manifestations. Some of our specimens display exclusively the albite type of twinning, some exclusively the pericline type, and others show both. The material examined by us is thus sufficiently extensive to prove or disprove the deductions from the theory. Actually, the observations support the theoretical inferences in the most complete and detailed fashion.

The existence of the two sets of reflections exhibiting the same colours but originating in different parts of the crystal is readily shown and the geometric relationship between them indicated by the theory simultaneously verified by the following procedure. The observer stands with his back to a window, the light from which falls on the specimen held in his hands with its polished face turned towards him. The orientation of the specimen required to display one of the coloured reflections is first ascertained by trial. It is also easy to locate the orientation in which the specimen exhibits the specular reflection from the platy inclusions lying with their faces parallel to

the 010 planes in the crystal. The observer then ascertains by trial, the position of an axis such that if the specimen is rotated about it, first the coloured reflection and then the specular reflection successively come into view. *A further rotation about the same axis and in the same direction brings the second reflection into view.* If the twinning is of the albite type, the axis of the rotation needed is found to be parallel to the composition planes of the twinning: it does not coincide with either the *a* or the *c*-axis of the crystal, but makes an angle of about 70° with the former. If the twinning is of the pericline type, the correct procedure for viewing the two reflections successively is to rotate the crystal about its *b*-axis through 180°. But since the *b*-axis is not far removed from being normal to the 010 planes of the crystal, a rotation in the same direction and about the same axis as in the case of the albite twinning is found to be effective.

Except in respect of colour which is identical for both reflections, the features they display are found to be different and indeed often strikingly different. That this is due to their location in different parts of the crystal is demonstrated by the exact correspondence between the disposition of the twinning layers at the surface through which the observations are made and the features exhibited by the iridescence. Actually, it is found that the angle at which the composition planes of twinning meet the polished face has a great influence. If they meet steeply, as in the case of pericline twinning, the iridescence exhibits alternate dark and bright bands traversing the surface, these interchanging places in the two sets of reflections. On the other hand, if the composition planes meet the external surface obliquely as in the case of the albite twinning, much depends on the disposition of the reflecting lamellæ in the alternate layers of the twinned crystal. If the reflecting lamellæ of one set are nearly parallel to the external face, those of the other set necessarily meet it obliquely; the reflection by the first set then appears almost uniform over the surface, while the reflection by the other set shows a banded structure. The degree of general transparency of the crystal plays a role of importance in deciding what is actually seen in any particular case; the greater the transparency, the more effective become the deeper layers in the crystal and the greater their contribution to the total observed luminosity. So much depends on the characters of the individual specimens that these details are best dealt with in describing their behaviour. This will be done later in the paper, and the particular cases illustrated in Plates I to V accompanying it will be fully commented upon.

The refractions at the external surface of a specimen occurring both at entry and at emergence of the light materially influence the settings of it required for observing the internal reflections. Except, however, when the

specimen has been inappropriately cut, the deviations in the course of the light rays produced by these refractions would not prevent the effects described above coming under observation. By immersing the specimen in a glass cell filled with a liquid having the same refractive index as labradorite, they may be completely eliminated. It is then possible to make a quantitative test of the geometrical relationship between the two sets of internal reflections indicated by the theory. Studies made in this way show that the settings at which the maximum intensity of iridescence is observed make an angle of 14° on one side or the other with that required for a specular reflection from the 010 planes of the crystal.

7. Phenomena Observed with Polarised Light

Some rather spectacular effects are observed when labradorite is illuminated by a beam of light which has passed through a polaroid sheet and the characteristic iridescence is viewed through a second polaroid sheet; the setting of the labradorite in its own plane, the angle of incidence of the light on it, and the setting of the two polaroids with respect to each other may be varied in the experiment, with interesting consequences. Apart from their experimental interest, the results observed with polarised light have a direct bearing on the problem of the structure of labradorite and the origin of its iridescence which forms the subject of this paper. Indeed, they afford further confirmation of the correctness of the theoretical approach made in the paper, as we shall presently proceed to show.

The reflection of electromagnetic waves which occurs at the boundary between two media is a consequence of the differences in their optical polarisabilities. When both media are crystalline and anisotropic, the intensity of such reflection would, in general, depend not only on the angle of incidence and state of polarisation of the incident light, but also on how the optic axes of the two crystals are orientated with respect to the direction of the electric vector in the incident waves. The state of polarisation of the reflected light would also depend on the same circumstances. As a consequence, the observable characters of the reflected light would, in general, exhibit a complex behaviour such as is not met with in the familiar case of optically isotropic media. In the present problem, however, we are concerned with the reflection of light at the boundary between two feldspars whose structures are similarly orientated in space, and this results in a great simplification, as we shall presently notice.

The second and third columns of Table I show the maximum and minimum refractive indices of labradorite and orthoclase respectively, while the fourth column shows the differences between them. It will be seen that the

TABLE I

	Ng	Np	Ng − Np	Ng′	Np′	Ng′ − Np′
Labradorite ..	1·5678	1·5598	0·008	1·565	1·559	0·006
Orthoclase ..	1·5260	1·5180	0·008	1·524	1·518	0·006
Differences ..	0·0418	0·0418	0	0·041	0·041	0

birefringence is of the same order of magnitude in the two feldspars and is quite small, while on the other hand, the differences in their refractive indices are several times larger. The fifth and sixth columns show the two refractive indices Ng′ and Np′ in each case for flakes lying on 010, while the seventh column gives the differences between them. It will be noticed that the lower index Np′ differs little from the minimum index Np in either case, and that the differences between Ng′ and Np′ are identical, in other words that the birefringence in flakes parallel to 010 is very similar in the two feldspars. Taking these facts into consideration, it is evident that the optical anisotropies would have a negligible effect on either the intensity or the state of polarisation of the light reflected at the boundaries of separation, which, as we have seen, make an angle of only 14° with the 010 planes in labradorite. In other words, we may, for the present purpose, treat the feldspars as optically isotropic media having refractive indices appropriate to the circumstances of each case. The following inferences are thus justified.

(*a*) The intensity of the internal reflections in labradorite would be sensibly independent of the setting of the crystal, if the angle of incidence remains unaltered.

(*b*) The internally reflected light would exhibit a polarisation of the normal type; this would be sensibly perfect for the Brewsterian angle of incidence on the reflecting layers, namely 44°, in other words, when the light is deviated through 88° by such reflection.

The two results stated above and especially the complete polarisation of the reflected light in a direction transverse to the incident beam indicated by the theory furnish us with an *experimentum crucis* for a test of its truth. It is satisfactory to note that the studies made by us fully confirm these results. To exhibit the polarisation effect, it is necessary to immerse the specimen in a square cell filled with a liquid having the same refractive index as labradorite, and to place it so that the light entering the cell through one face and reflected within the specimen emerges through the perpendicular face. It is also necessary to arrange that the polarisation due to the internal reflection is

not modified by the birefringence of the labradorite. This may be secured by a suitable orientation of the specimen within the cell. For the same reason, it is preferable to employ a specimen that does not exhibit twinning, at least in the immediate vicinity of the area under observation. It is found that in these circumstances, the reflected light is completely quenched when observed through a polaroid set with its vibration direction in the plane of incidence.

The phenomena exhibited by labradorite when illuminated by polarised light and observed through a polariser owe their interest to the fact that they render the presence of the twinning layers adjacent to the surface as well as their inclination to the latter directly accessible to observation. The phenomena are best described when dealing with the behaviour of our individual specimens.

8. Spectral Characters of the Iridescence

When we compare the iridescence of labradorite with the colours of thin plates, we notice certain obvious similarities as well as some striking differences. A regular colour sequence is exhibited by some specimens of labradorite, recalling those shown by soap films of varying thickness or by Newton's rings. Boggild (*loc. cit.*) describes some fine examples. The colours also change with the obliquity of observation in much the same way as the colours of thin films. The spectral nature of the colours is, however, wholly different in the two cases. We do not observe with labradorite the dark and bright bands alternating in the spectrum characteristic of the interferences of thin plates; what is actually the observed is a continuous variation of intensity in the spectrum. Particularly significant is Boggild's remark that the colours of the first order which are a prominent feature in Newton's rings are wholly absent in the case of labradorite. These begin with a blue which is far richer than the faint blue of the first order, and are followed by other rich colours and not by the white observed in the Newtonian sequence.

The facts stated find a natural explanation in the ideas developed in the present paper. As we have seen, the optical heterogeneity of labradorite owes its origin to the orthoclase or potash feldspar present segregating itself from the albite-anorthite. The first stage of such segregation would evidently be the formation of very small crystallites distributed throughout the volume of the crystal. Such segregation would evidently give rise to a Tyndall effect in which the shorter wave-lengths would predominate, and hence having the rich blue colour characteristic of the scattering of light by small particles. Since the particles occupy fixed positions, the diffused radiations would have specifiable phase-relations and would be capable of mutual interference.

The observed effect in any direction would depend on the disposition of the particles in space. In view of the similarities in chemical composition and crystal structure between orthoclase and albite-anorthite, it is scarcely to be supposed that such disposition would be wholly random in character. If, as may reasonably be assumed, the diffracting particles locate themselves more or less accurately in sets of planes having a specific orientation within the crystal, the optical effect resulting from the passage of a beam of light would be a diffusion, the intensity of which would be greatest around a particular direction; it may be described as a diffuse reflection by the set of planes referred to. At a later stage in the segregation, the particles would be crystallites no longer small in comparison with the wave-length of light. Assuming, for the reasons discussed earlier in the paper, that they are lamellæ having a specific orientation, the colour of the diffracted light would be determined by their thickness, while its angular extension would depend on their other dimensions. This second stage could scarcely be reached unless the dimensions of the crystallites are much in excess of those required to give interference colours of the first order in the Newtonian scale.

The foregoing remarks may be summed up by the statement that the colours of labradorite are neither a simple Tyndall diffusion nor a simple case of thin-film colour; they are a case *sui generis* in which the optical principles underlying both of these phenomena play a part. We may conclude this section by a brief description of some effects which we have observed and which are readily understood in the light of this statement. As both Rayleigh (*loc. cit.*) and Boggild (*loc. cit.*) have mentioned, the coloured reflections in labradorite are not sharply defined but appear spread out over a range of angles. We have noticed in our studies that the angular range of this spread is about twice as great for a blue iridescence—despite the smaller wave-lengths—as for a red or an orange iridescence with its greater wave-lengths. We have noticed also that when a specimen exhibiting varied colours over its area is illuminated and is slowly turned away from the setting at which the reflection is brightest, the areas of blue iridescence continue to be visible long after the other areas are dark. Further, we have noticed in the same circumstances that the areas exhibiting these other colours show a distinct change of tint towards the blue before they are finally extinguished.

9. Some Typical Examples

In the preceding sections of the paper, references were made in general terms to the results of our observations with the specimens of labradorite at our disposal. By way of supplementing these references and to give them substance, we shall proceed to describe in some detail, the individual behaviour of a few of them.

Specimen No. 1 is our largest and finest piece. It is a slab some 24 centimeters long, 12 centimetres broad and of thickness about a centimetre at one end, thinning off to five millimeters at the other. It was obtained through the East Coast Mineral Corporation of New York, and the locality of its origin is shown on its label as the Grenfell quarry, Nepoktulegatsuk, Tabors Island, near Nain, Labrador. Though apparently dark in colour, the material is fairly transparent and exhibits a brilliant blue iridescence on both faces. One of the faces had been polished, evidently to exhibit the effect to the greatest advantage, but the other, though quite rough, showed the same colour with scarcely less brilliance. The material on careful scrutiny shows a wavy discontinuity running through it. The central part of the slab displays a bright blue colour, while the areas to the left and the right exhibit a darker and deeper blue. Except in this respect, the iridescence is seen to possess a most remarkable uniformity over the entire area of the specimen.

Fig. 1 in Plate I is a photograph of the specimen when displaying its characteristic iridescence. The illumination of the slab was a few degrees away from the normal to avoid reflection from the external surface. Fig. 2 is another photograph taken with the specimen turned to such a position that the aventurism due to inclusions lying in the 010 planes is prominently displayed. This effect varies enormously in its brightness over the area of the specimen, and is in fact almost entirely concentrated in and around the areas in which there are visible defects or breaks in the material. Fig. 3 is a photograph exhibiting the second internal reflection observed in the specimen when it is held with the light falling on it rather obliquely, in a direction running from left to right in the picture and viewed in nearly the same direction. This reflection, unlike that reproduced in Fig. 1, shows a great many bands running parallel to each other across the specimen. Holding the specimen in his hand and rotating it about an axis parallel to the general direction of these bands, the observer can view successively the banded reflection, the aventurine reflection, and the uniform reflection, reproduced as Figs. 3, 2 and 1 respectively in Plate I.

Examining the edge of the slab where the 001 cleavage could be seen, it became evident that the slab was traversed in a direction parallel to the 010 planes of the crystal by a whole series of twinning bands of the albite type. It was verified that at every one of the twinning lamellæ, and exactly along the line of its meeting with the polished face of the specimen, one of the bands shown in Fig. 3, Plate I, was located. The colour of the bands was exactly the same as that of the iridescence exhibited in Fig. 1 of Plate I, namely bright blue in certain areas and a deeper blue in the other areas. The thinness of the twinning layers is evidently responsible for the fineness of the bands seen

in Fig. 3. The observer readily notices that the banded reflections are more steeply inclined to the polished face of the specimen than the twinning layers themselves, though they arise in the latter. Very faint dark lines can be seen in Fig. 1 along the intersections of the twinning bands with the polished surface of the specimen, showing thereby that in the first reflection, these regions remain dark.

Fig. 1 and Fig. 2 in Plate II are photographs of the same specimen illuminated almost normally by a beam of light which has passed through a polaroid, and viewed nearly normally by the internally reflected light through a second polaroid. Fig. 1 represents the case in which the two polaroids are crossed and Fig. 2, the case in which they are parallel. The bands seen traversing the face of the specimen in these photographs appear and disappear periodically four times in each revolution when the specimen is turned round in its own plane. It is clear that these effects arise from the birefringence of the crystal acting jointly with the birefringence of the twinning layers running through it and meeting the surface obliquely. We get bright lines in Fig. 1 and dark lines on Fig. 2 at the places where the twinning layers meet the surface, because at these places, the birefringence in the twinning layers affects the reflected light from the maximum depth in the illuminated specimen. It may be mentioned that somewhat analogous phenomena, though much less striking, may be seen when unpolarised light is incident on the slab rather obliquely and the reflected light is viewed through a polaroid. The internal reflection itself acts as a polariser in this case.

Figs. 3 and 4 in Plate II illustrate different kinds of inclusions observed in labradorite which are responsible for the aventurine reflections.

A few words must suffice for each of our other specimens illustrated in the Plates accompanying the paper.

Specimen 2 is a typical example of multiple twinning of the pericline type. It exhibits a greenish yellow iridescence. Here the twinning layers meet the polished face of the specimen almost normally. Figs. 1 and 3 in Plate V show its two internal reflections; it is possible to make out that the dark and bright bands have interchanged places in them. Fig. 2 is a photograph of the same specimen held in such a position that neither iridescence is visible.

Specimen 3. *See Figs.* 4, 5 *and* 6 *in Plate III.*—These illustrate respectively the first coloured reflection, the aventurine reflection and the second coloured reflection in the specimen. The iridescence is a golden yellow, changing to green and greenish blue at oblique incidences. The banding

seen very prominently in Fig. 4 and less clearly in Fig. 6 is due to the albite twinning layers meeting the surface obliquely.

Specimen 4. *See Figs.* 1, 2 *and* 3 *in Plate III.*—This specimen exhibits a blue iridescence except towards the left where there are patches of opacity interspersed with areas of iridescence in which varied colours appear. The horizontal bands in the upper part are due to the pericline twinning, while the inclined bands towards the right owe their origin to the albite type of twinning. Figs. 1 and 3 illustrate respectively the two coloured reflections, and are seen to be complementary, the bright areas in one being the dark areas in the other and *vice versa*. Fig. 2 represents the aventurine reflection by the specimen.

Specimen 5. *See Figs.* 6, 7 *and* 8 *in Plate IV.*—These represent respectively, the first coloured reflection, the aventurine reflection and the second coloured reflection. The banding in Figs. 6 and 8 is due to the albite twinning, and the positions of the dark and bright bands in them are seen to be complementary to each other. Fig. 5 in Plate IV shows the same specimen viewed under incident polarised light through a second polaroid in the crossed position. It should be mentioned that this specimen exhibits very varied colours over its area; bright blue in the regions both around the dark centre and also towards its margins, with yellow, orange and red bands succeeding each other in the intervening areas.

Specimen 6. *See Figs.* 5, 6 *and* 7 *in Plate II.*—This is a small but beautiful piece which exhibits a peacock-blue iridescence with orange-yellow spots prominently in one setting (Fig. 5). In the other setting (Fig. 7), the iridescence shows peacock-blue patches which are much less intense; these appear in areas which are either completely dark or else rather faint in Fig. 5. Very striking also are the bright lines seen in Fig. 7 in the positions where the dark lines appear in Fig. 5. These lines represent pericline twinning bands meeting the surface steeply. Elsewhere, the specimen shows albite twinning, with one set of the iridescent laminæ almost parallel to the surface and giving the strong reflection seen in Fig. 5, while the other set is more steeply inclined to the surface and gives the feeble effect appearing in Fig. 7.

Specimen 7. *See Figs.* 1, 2, 3 *and* 4 *in Plate IV.*—This is rather an extraordinary piece, showing several separate crystals in different settings firmly adhering to each other. The four photographs show its iridescence under different angles of illumination and observation. The central area shows the albite type of twinning, while two others show the pericline twinning, as is evident from the sharply defined dark and bright bands crossing the

iridescent areas. The interchange in the positions of these over the area of the crystal on the left is clearly visible on a comparison of Figs. 2 and 4.

In concluding this paper, we have to express our grateful thanks to those whose help has enabled us to bring this investigation to a successful conclusion. Several of our labradorite specimens were a very generous gift from Mr. B. W. Anderson of London. Specimens of other varieties of feldspars presented to us by Professor T. N. Muthuswami of Madras, Dr. C. Mahadevan of Waltair and Mr. L. S. Krishnamurthy of Hyderabad also proved very useful in our studies. The Director of the Geological Survey in Mysore, Dr. C. S. Pichamuthu materially assisted us in getting access to the mineralogical literature on feldspar. Mr. T. K. Srinivasan, Government of India Senior Scholar in Mineralogy at this Institute, has been very helpful to us in the study of this literature.

Summary

General considerations indicate that the phenomenon of labradorescence owes its origin to the segregation of potash feldspar as crystallites or lamellæ of orthoclase which remains embedded in an albite-anorthite matrix and give rise to optical heterogeneity. The following are derived as theoretical consequences of such segregation and have been confirmed by observations made with a representative collection of specimens.

(A) Labradorite which is multiply twinned according to either the albite or pericline law or both, exhibits its characteristic reflections in two different settings geometrically related to each other by the twinning law. The two reflections display identical colours, but have their origins in different parts of the crystal, and this makes itself evident as a visible banding in one or the other or both of the reflections.

(B) The light reflected transversely to the incident beam is completely polarised.

(C) The intensity of the reflected light is independent of the setting of the reflecting layers in their own plane.

(D) The spectral character of the reflected light would approach that of a Tyndall diffusion when the crystallites are very small. Hence the colours of the first order in the Newtonian sequence would not be observed. The spectral character and the colour sequence at the later stages of segregation would also be different from those of thin films.

(E) The angular spread of the reflected light is greatest for the blue iridescence and less for other colours such as yellow, orange and red.

The effects arising when labradorite is illuminated and observed by polarised light are also described and explained in the paper.

Numerous photographs reproduced in five plates illustrate the observed phenomena.

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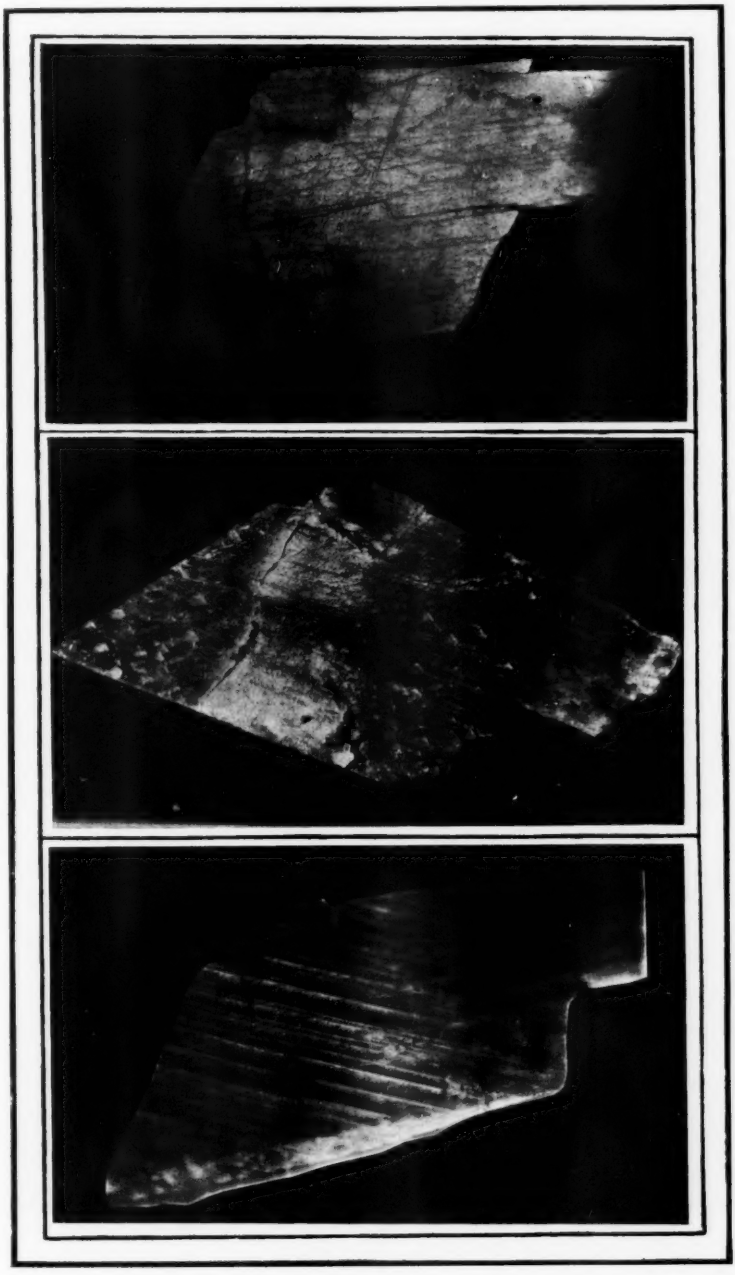

FIG. 1

FIG. 2

FIG. 3

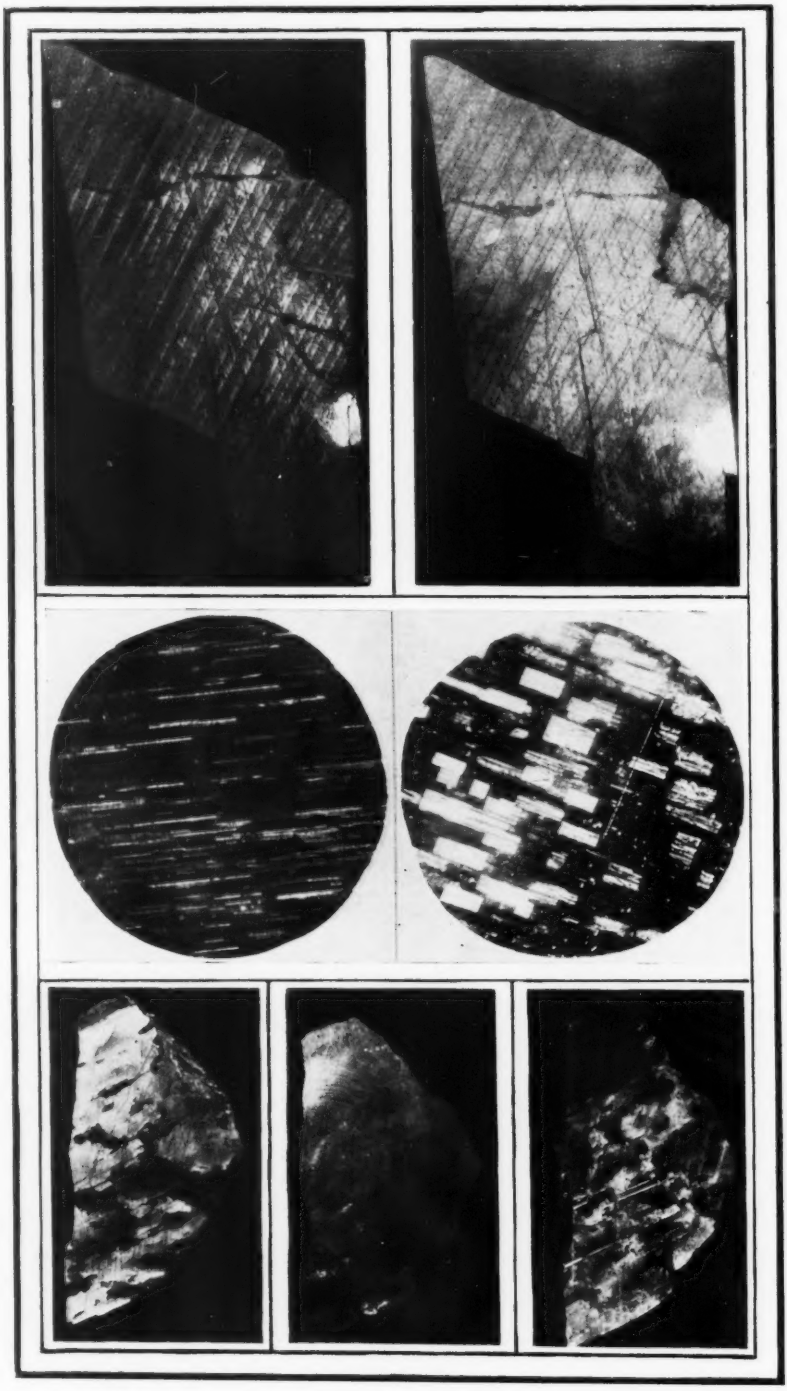

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

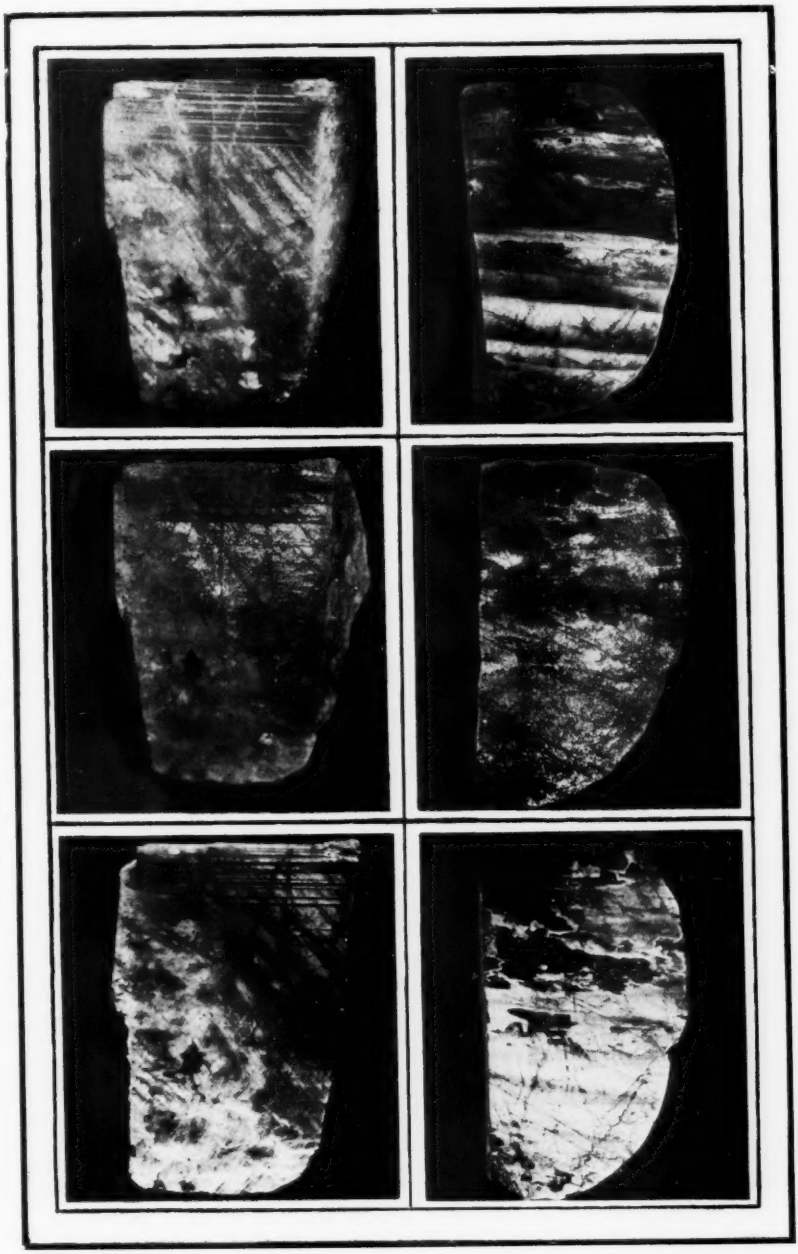

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 1

FIG. 2

FIG. 3

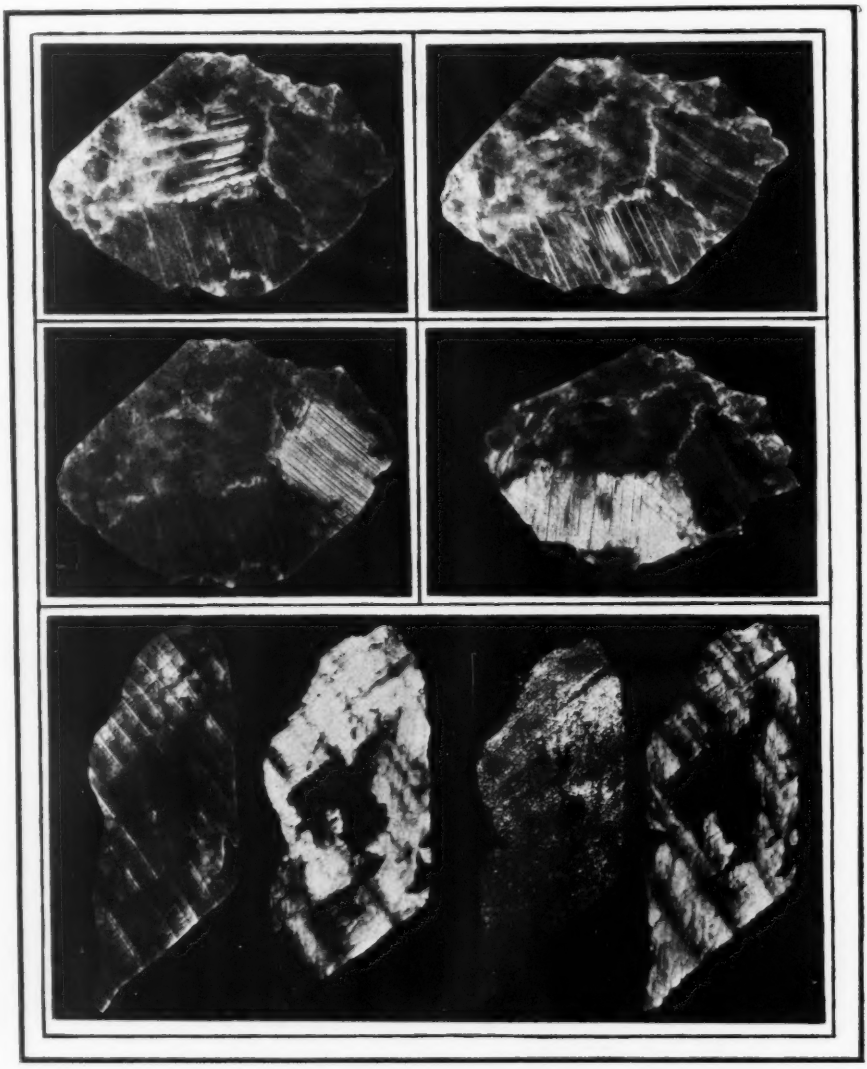

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

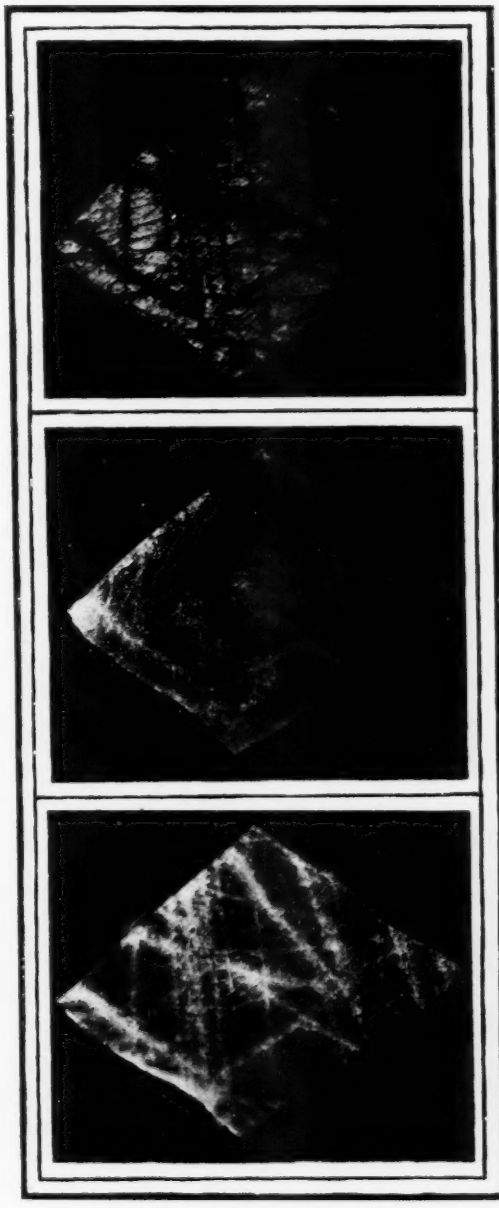

FIG. 1

FIG. 2

FIG. 3

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XII. A Synthesis of 7-O-Methyl-Ethers of Hydroxy Flavones

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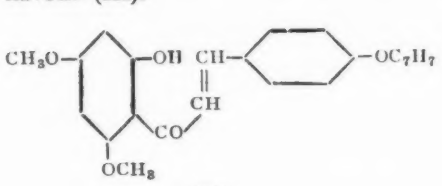
Received April 10, 1950

Partial methyl ethers of flavones and flavonols are found to occur widely in nature and a large number of them are 7-methyl ethers, the 7-position being very frequently subjected to methylation analogous to glucoside formation. Based on past work a few methods could be suggested for the synthesis of these 7-methyl ethers. (1) Direct synthesis (Allan-Robinson) from the appropriate components has been employed by Kuhn and Low[1] for obtaining rhamnetin. But it has not been more widely adopted in view of inherent difficulties; the yields are very discouraging in the preparation of flavone derivatives. (2) Partial methylation of hydroxy flavones has been successful only in the case of chrysin to yield tectochrysin.[2] (3) On the other hand partial demethylation of more fully methylated methyl ethers which are readily obtained in synthesis has been more successfully adopted (tectochrysin and genkwanin; izalpinin and rhamnocitrin[3, 7]). For this purpose several reagents have been employed; aluminium chloride, aluminium bromide and hydrobromic acid under suitable conditions hydrolyse ether groups in the 5 and 3 positions. In certain cases where demethylation of 5 and 8 positions are involved nitric acid could also be employed.[4] It forms a quinone which could subsequently be reduced to the quinol, *e.g.*, isowogonin.

As already mentioned the above methods are successful only in simpler cases, but fail in the preparation of more complex types. The discovery of new methods which are suitable for such cases should mean valuable addition to technique. One such suggested itself as the result of our recent work. It consists in making the 7-methyl ether of the corresponding flavanone and subsequently oxidising it to the flavone. In our studies on the partial demethylation of chalkones[5] it was shown that by employing hydrobromic acid (48%) at 100° it is possible to prepare hydroxy flavanone 7-methyl ethers. In a subsequent paper on the iodine oxidation of flavanones[6] the conversion of these into corresponding flavones has been described. The two put together provide a new and convenient method for the synthesis of

7-methyl ethers of hydroxy flavones. As a typical example the case of genkwanin (I) is described in the following para:

Genkwanin (I) which is the 7-methyl ether of apigenin was first synthesised by Mahal and Venkataraman[7] by the dehydrogenation of 2-hydroxy-4:6-dimethoxy-4′-benzyloxy chalkone (II) with selenium dioxide and by the subsequent debenzylation and partial demethylation of the resulting flavone (III).



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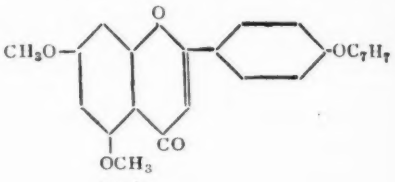
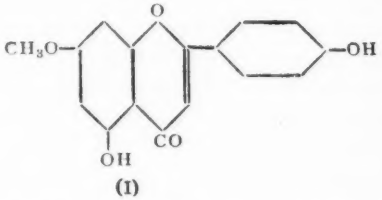
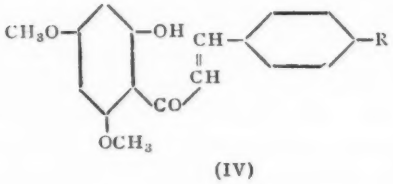


(III)



(I)

The new method consists in making sakuranetin (V, R = OH) from 2-hydroxy 4:6:4′-trimethoxy chalkone (IV, R = OCH_3), by heating it with hydrobromic acid[5] and subsequently dehydrogenating the resulting sakuranetin with iodine.[8] The yields are good. This method has now been extended to closely related flavones. Tectochrysin (VI, R = H) is now made from



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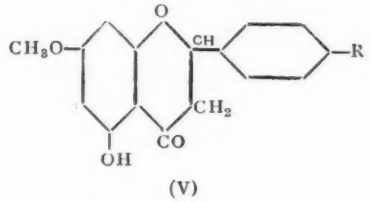

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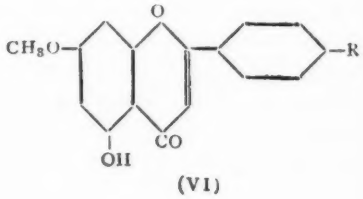
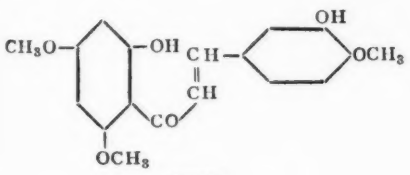


(VI)

2-hydroxy-4: 6-dimethoxy chalkone (IV, R = H), the intermediate stage being 5-hydroxy-7-methoxy flavanone (V, R = H).

7-Methyl ether of luteolin (VII) is an example of a flavone methyl ether which is rather difficult to prepare by using the other methods. Diller and Kostanecki[9] obtained in the course of their demethylation of luteolin-5: 7: 3′-trimethyl-4′-ethyl ether besides luteolin, a by-product melting at 270°. They considered it to be the 7-methyl ether but the point does not seem to have been adequately investigated. The 7-methyl ether is readily obtained by the new procedure. For this purpose 2-hydroxy-4: 6-dimethoxy acetophenone is condensed with isovanillin in presence of alkali. The resulting chalkone (VIII) yields readily 7-O-methyl eriodictyol (IX) on treatment with hydrobromic acid. Subsequent dehydrogenation with iodine proceeds smoothly to produce 7-O-methyl luteolin (VII). As a variation the condensation of phloracetophenone dimethyl ether with the dibenzoate of protocatechuic aldehyde has also been effected in the presence of hydrogen chloride in ethyl acetate solution.[10] The resulting chalkone (X) undergoes both demethylation and debenzoylation with hydrobromic acid to yield 7-O-methyl eriodictyol (IX). Of the two methods the use of isovanillin is more convenient. The melting point of 7-O-methyl luteolin thus obtained is found to be 258–60°.



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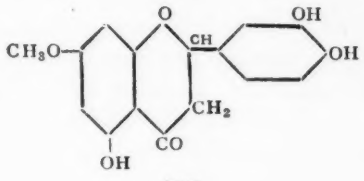
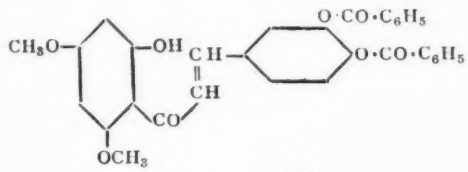
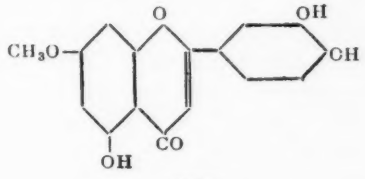


(IX)



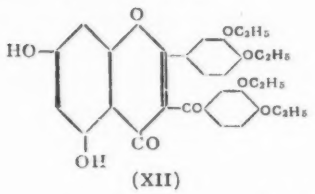
(X)



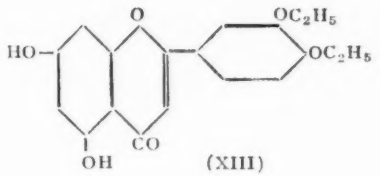
(VII)

Though the 7-methyl ethers of eriodictyol and luteolin have not so far been isolated from natural products their occurrence seems to be possible. They correspond to rhamnetin in the flavonol series. Recently Ferguson *et al.*[11] considered that the muscle inhibiting compound in lucerne was luteolin-7-methyl ether; it has been subsequently found to be a different flavone.[12] Further the melting point of our methyl ether of luteolin differs from that of

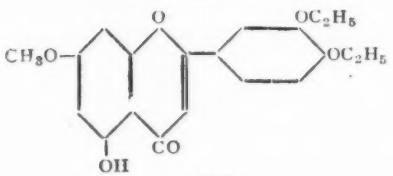
the demethylation experiments of Diller and Kostanecki.[9] For these reasons it was felt necessary to confirm the constitution of the synthetic material; the flavone methyl ether has therefore been fully ethylated using ethyl sulphate. The product is found to be identical with 7-methoxy-5: 3′-4′-tri-ethoxy flavone (XI) which has been independently synthesised in the following manner. Phloracetophenone is condensed with the anhydride and sodium salt of diethyl protocatechuic acid (Allan-Robinson). The major product appears to be the 3-acyl derivative (XII) which is hydrolysed to luteolin-3′: 4′-diethyl ether (XIII). This is subsequently subjected to partial methylation in 7-position (XIV) and final ethylation in the 5-position to yield the required product (XI).



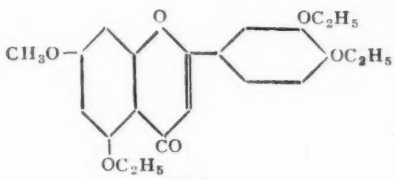
(XII)



(XIII)



(XIV)



(XI)

Experimental

Tectochrysin (VI, R = H)

The preparation of 5-hydroxy-7-methoxy flavanone (V, R = H) has already been reported.[5] It (0·5 g.) was dissolved in alcohol, sodium acetate (2 g.) added and the solution boiled. To this a boiling solution of iodine (0·5 g.) in alcohol was added with shaking. Iodine was rapidly decolourised and in the end there was a permanent colour due to iodine. On cooling, the flavone crystallised out. It was filtered and recrystallised from alcohol when it separated out in the form of pale brown shining needles melting at 165-6°. The mixed melting point with an authentic sample of tectochrysin[2] was undepressed. Some more of tectochrysin could be obtained by concentrating the alcoholic solution and crystallising the product from alcohol. Yield, 0·35 g.

2: 3′-*Dihydroxy*-4: 6: 4′-*trimethoxy chalkone* (*VIII*)

A mixture of 2-hydroxy 4: 6-dimethoxy acetophenone (2 g.) and isovanillin (2·5 g.) was dissolved in alcohol (70 c.c.) and potassium hydroxide

(5 g. in 5 c.c. water) added to it with cooling under the tap. The solution was then kept corked for 48 hours at room temperature. It was then diluted with water (200 c.c.), cooled and acidified with hydrochloric acid. The precipitated solid was filtered and washed twice with sodium bicarbonate solution to remove the isovanillic acid present in it. On crystallising it from alcohol 2:3′-dihydroxy-4:6:4′-trimethoxy chalkone (VIII) separated in the form of bright yellow rectangular prisms melting at 193–4°. It gave a deep brown colour with ferric chloride in alcoholic solution and dissolved readily in sodium hydroxide solution. Its alcoholic solution gave no colour with magnesium and hydrochloric acid. (Found: C, 65·2; H, 5·5; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5%.)

7-O-Methyl-eriodictyol (*7-methoxy*-5:3′:4′-*trihydroxy flavanone*) (*IX*)

The above chalkone (1 g.) was dissolved in glacial acetic acid (5 c.c.) and treated with a saturated solution of hydrobromic acid in acetic acid (10 c.c.). The mixture was then heated on a boiling water-bath for 1½ hours, cooled and diluted with water and left in the refrigerator overnight. The solid that separated was filtered and washed with water. It was crystallised first from ethyl acetate-petroleum ether mixture and then from alcohol. It finally came out in the form of colourless needles melting at 215°. It gave a green colour with ferric chloride in alcoholic solution and a blue colour with concentrated nitric acid. On reduction with magnesium and hydrochloric acid in alcoholic solution it developed a bright scarlet colour. Some more of it could be obtained by ether-extracting the aqueous solution and evaporating the ether, after washing with aqueous sodium bicarbonate. Yield, 0·4 g. (Found: C, 61·9; H, 4·9; OCH_3, 10·3; $C_{16}H_{14}O_6$, $\frac{1}{2}H_2O$ requires C, 61·7; H, 4·8; OCH_3, 10·0%. Loss on drying: 3·3; $C_{16}H_{14}O_6$, $\frac{1}{2}H_2O$ requires 2·9%.)

7-O-*Methyl luteolin* (*VII*)

7-O-Methyl eriodictyol (0·5 g.) was treated with sodium acetate (2 g.) and iodine (0·5 g.) in alcoholic solution as described earlier. 7-O-Methyl luteolin crystallised from alcohol in the form of small yellow prisms melting at 258–60°. Its alcoholic solution gave a green colour with ferric chloride and a red colour with magnesium and hydrochloric acid. (Found: C, 63·8; H, 4·0; OCH_3, 10·7; $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0; OCH_3, 10·3%.)

2-*Hydroxy*-4:6-*dimethoxy*-3′:4′-*dibenzoyloxy-chalkone* (*X*)

A solution of phloracetophenone-4:6-dimethyl ether (1 g.) and dibenzoate of protocatechuic aldehyde (1·8 g.) in dry ethyl acetate was cooled in

ice, saturated with dry hydrogen chloride gas for 2 hours, and kept at 0° for 24 hours. Ethyl acetate was then distilled under reduced pressure. The solid that was left behind was crystallised from excess of alcohol when it was obtained in the form of pale brownish yellow prisms melting at 168–70°. It gave a reddish brown colour with ferric chloride in alcoholic solution. Yield, 0·6 g. (Found: C, 70·6; H, 4·3; $C_{31}H_{24}O_8$ requires C, 71·0; H, 4·5%.)

7-O-*Methyl-eriodictyol*

The above chalkone (1 g.) was dissolved in glacial acetic acid (7 c.c.) and a saturated solution of hydrogen bromide in glacial acetic acid (15 c.c.) added to it. The mixture was heated on a water-bath for 1 hour and after cooling, was diluted with water and left in the ice-chest overnight. The solid that separated was filtered and washed twice with aqueous sodium bicarbonate and then with water. When crystallised twice from alcohol (animal charcoal) it came out in the form of colourless needles melting at 215–16°. It gave a green colour with ferric chloride in alcohol and a blue colour with conc. nitric acid. On reduction with magnesium and hydrochloric acid it developed a scarlet red colour. It agreed in all its properties with the sample described earlier and the mixed melting point was undepressed.

5 : 7-*Dihydroxy*-3′ : 4′-*diethoxy flavone* (*XIII*)

Phloracetophenone (3 g.), diethyl protocatechuic anhydride (25 g.) and the sodium salt of diethyl protocatechuic acid (5 g.) were intimately mixed and heated for 3 hours at 180–90° under reduced pressure. The product was refluxed with alcoholic potash (6 g. in 75 c.c.) for 20 minutes, alcohol removed under reduced pressure, the residue dissolved in water and carbon dioxide passed through it. The 3-acyl derivative that separated was filtered and washed with water. It crystallised from alcohol in the form of brownish yellow prisms melting at 190° (decomp.). It was hydrolysed by refluxing with aqueous sodium carbonate (5%, 100 c.c.) for 2 hours. The carbonate solution was cooled and acidified with hydrochloric acid. The solid that separated was filtered and washed with sodium bicarbonate solution to remove the acid formed (solution A). The remaining flavone crystallised from ethyl acetate-alcohol mixture in the form of colourless short rectangular prisms melting at 250–52°. Its alcoholic solution gave a reddish violet colour with ferric chloride and a bright red colour with magnesium and hydrochloric acid. It dissolved readily in aqueous sodium carbonate. (Found: C, 66·6; H, 5·4; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%.) The sodium bicarbonate solution (A) on acidification gave diethyl protocatechuic acid (m.p. and mixed m.p. 165–6°).

Partial methylation

The above flavone (0·5 g.) was refluxed for 6 hours with dimethyl sulphate (0·15 g.) and anhydrous potassium carbonate (0·5 g.) in acetone solution (40 c.c.). It was then filtered and the residue washed with acetone. The acetone filtrate was then evaporated and the product crystallised. 5-Hydroxy-7-methoxy-3′: 4′-diethoxy-flavone (XIV) crystallised from alcohol in the form of colourless prisms and needles melting at 155–6°. (Found: C, 66·9; H, 5·7; $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·6%.) It gave a brown colour with ferric chloride in alcoholic solution and was sparingly soluble in aqueous sodium hydroxide.

Ethylation

The above flavone (XIV) (0·3 g.) was ethylated with excess of diethyl sulphate (0·4 c.c.) and anhydrous potassium carbonate by refluxing in acetone solution for 24 hours. 7-O-Methyl-triethyl luteolin (XI) crystallised from alcohol in fine colourless needles melting at 162–3°. It gave no colour with ferric chloride in alcoholic solution and was insoluble in aqueous sodium hydroxide. (Found: C, 68·4; H, 6·5; $C_{24}H_{26}O_2$ requires C, 68·7; H, 6·3%.)

Ethylation of 7-O-methyl luteolin

The synthetic sample of 7-O-methyl luteolin (0·2 g.) was ethylated by refluxing it for 24 hours with excess of diethyl sulphate (0·5 g.) and anhydrous potassium carbonate (2 g.) in acetone solution. The product crystallised from alcohol as colourless needles melting at 162–3°. It agreed in all its properties with 7-O-methyl-triethyl luteolin described above and mixed melting point was undepressed.

Summary

A general method for the synthesis of the 7-methyl ethers of hydroxy flavones is described using as examples (1) tectochrysin, (2) genkwanin and (3) 7-O-methyl luteolin. It consists in preparing the corresponding 7-O-methyl flavanone and oxidising it with iodine. 7-O-Methyl eriodictyol is now made from (*a*) 2: 3′-dihydroxy-4: 6: 4′-trimethoxy chalkone and (*b*) 2-hydroxy-4: 6-dimethoxy-3′: 4′-dibenzoyloxy chalkone by treatment with hydrobromic acid. Iodine oxidation of it yields (3). The constitution of this product is confirmed by fully ethylating it and showing that the triethyl ether is identical with 7-methoxy-5: 3′: 4′-triethoxy flavone.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXIX. A Note on the Synthesis of 3-Methyl-Gallic and Myristicic Acids

By T. R. Seshadri, F.A.Sc., and T. R. Thiruvengadam

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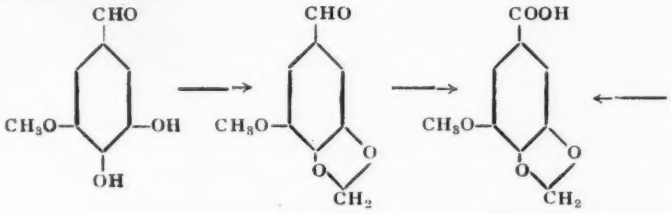
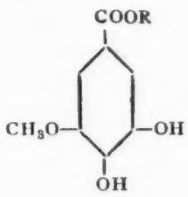
Received April 10, 1950

Myristicic acid (III) was first synthesised by Baker[1] by the methylenation of 3-methyl-gallic aldehyde (I) and subsequent oxidation. An improved method of methylenation was used by Rao and Seshadri[2] and this considerably increased the yields. An alternative method would be to methylenate 3-methyl gallic acid (IV, R = H) itself. This has now been satisfactorily worked out. The acid is first esterified and the crude ester (IV, $R = C_2H_5$) methylenated with methylene iodide and potassium carbonate in dry acetone medium and the product subsequently saponified. A yield of about 60% of myristicic acid is obtained.



(I) (II) (III)

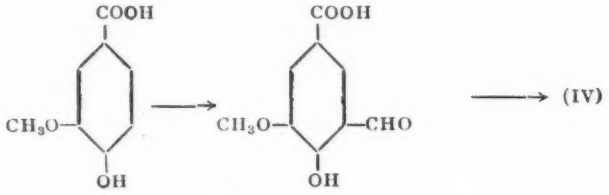


(IV)

3-Methyl-gallic acid (IV, R = H) required for this purpose was first made by Vogl[3] starting from vanillin and passing through a number of stages. The melting point was recorded as 200° which is too low. Subsequently Fischer[4] made it from gallic acid, first making the carbonato

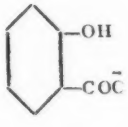
derivative using phosgene, subsequently methylating it and hydrolysing the carbonato group. Later Bradley, Robinson and Schwarzenbach[5] modified this procedure employing dichlorodiphenylmethane instead of phosgene. They also pointed out that the correct melting point of this substance is 220° and the melting point 131–132° given by Shriner and McCutchan[6] was due to an error owing to the mistaking of 3-methyl gallaldehyde for this acid.

The above 3-methyl-gallic acid (IV, R = H) has now been made by adopting the two-stage method of nuclear oxidation, analogous in procedure to the recent synthesis of hydroxy eugenol.[7] Vanillic acid (V) is used for this purpose. By the action of hexamine an aldehyde group is introduced in the 5-position (VI) which undergoes smooth oxidation with hydrogen peroxide to give a good yield of the required acid (IV). Its identity is established not only from its properties, but also by methylation to trimethyl gallic acid.



(V) (VI)

The above experiments constitute a typical example for the suitability of this method of nuclear oxidation even when carboxyl groups are present. Such groups, present para or ortho to phenolic hydroxyl groups, have been found in test experiments to be unaffected in Dakin's reaction. A discussion of this reaction has been given in a recent publication.[8] The non-reactivity of the carboxylic acids could be attributed to the lack of development of the adequate degree of positive charge on the carbon atom belonging to the carboxyl group. In alkaline medium the negative charge on the carboxylate ion (VII) may be expected to produce this adverse effect and it will be absent in the corresponding aldehydes and ketones.



(VII)

Experimental

Vanillic acid-5-aldehyde (VI)

Vanillic acid (3 g.) and hexamine (12 g.) were dissolved in hot glacial acetic acid (22·5 c.c.) and the clear yellow solution was heated on a boiling water-bath for six hours. Boiling hydrochloric acid (1 : 1, 30 c.c.) was then added and the heating continued for half an hour more. The yellow crystals of vanillic acid-5-aldehyde, obtained on cooling the solution, were recrystallised from alcohol to give yellow needles melting at 223–4°. Yield 1 g. It was soluble in sodium carbonate and sodium hydroxide solutions. It gave a pink colour with alcoholic ferric chloride. (Found: C, 54·8; H, 4·3; $C_9H_8O_5$ requires C, 55·1; H, 4·1%.) (Tiemann and Mendelsohn[9] who adopted the Reimer-Tiemann method gave the melting point as 221–2°.)

Oxidation of vanillic acid-5-aldehyde. Preparation of 3-methyl-gallic acid (IV, R=H)

The aldehyde (1 g.) was dissolved in normal alkali (7·8 c.c.) and pyridine (3 c.c.). Hydrogen peroxide (6%, 4 c.c.) was added to the cooled solution drop by drop. It was then left aside for two hours. The solution, after acidifying with hydrochloric acid, was saturated with sodium chloride and extracted with ether and the extract washed with dilute hydrochloric acid. On evaporating the solution, 3-methyl gallic acid was left behind as a brown crystalline solid. It was crystallised from a mixture of ethyl acetate and benzene to give almost colourless needles melting at 221° (decomp.) Yield 0·8 g. It gave a bluish violet colour with alcoholic ferric chloride.

Trimethyl gallic acid

The dihydroxy acid (0·2 g.) was methylated with dimethyl sulphate (0·3 c.c.) and sodium hydroxide (1 N; 5 c.c.). After heating for half an hour on the water-bath the solution was acidified and the crystalline precipitate formed was filtered and recrystallised from hot water when it was obtained in the form of colourless needles melting at 167°. Mixed melting point with an authentic sample of trimethyl gallic acid was not depressed.

Myristicic acid (III)

The dihydroxy acid (IV, R = H) (1·0 g.) was esterified by refluxing with absolute alcohol (3 c.c.) and a few drops of concentrated sulphuric acid for two hours. Water was then added when the ester (IV, $R = C_2H_5$) separated as a pale brown liquid. It was extracted with ether and the ether extract washed with aqueous sodium carbonate and dried over anhydrous

sodium sulphate. The solvent was then distilled off and any traces of alcohol present were removed under reduced pressure.

The dry residue was methylenated by refluxing in anhydrous acetone solution (50 c.c.) with methylene iodide (2 c.c.) and anhydrous potassium carbonate (8 g.) for 12 hours. The solution was then filtered and the solvent distilled off. Any traces of methylene iodide were removed under reduced pressure over a water-bath. The residue was dissolved in ether and the ether solution washed with aqueous sodium hydroxide and then with water. The ether was then removed by distillation and the ester left behind was hydrolysed by refluxing for half an hour with alcoholic potash. The alcohol was then distilled off and the residue treated with dilute hydrochloric acid. The crystalline precipitate thus obtained was filtered and recrystallised from aqueous alcohol when it was obtained in the form of colourless needles melting at 210°. Yield 0·6 g. It gave a yellow colour with concentrated sulphuric acid and an emerald green colour with gallic acid and concentrated sulphuric acid which gradually changed to bluish green. Mixed melting point with an authentic sample of myristicic acid obtained from natural myristicin was not depressed.

Summary

3-Methyl-gallic and myristicic acids have been synthesised by new methods. For this purpose vanillic acid is converted into its 5-aldehyde and oxidised with alkaline hydrogen peroxide to yield 3-methyl-gallic acid. Esterification, methylenation and hydrolysis give rise to a good yield of myristicic acid.

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ANTHRAQUINONE AND ANTHRONE SERIES*

Part III. Constitution of Dinitrodibenzanthrone and Some Derivatives of 3 : 3′-Dibenzanthronyl

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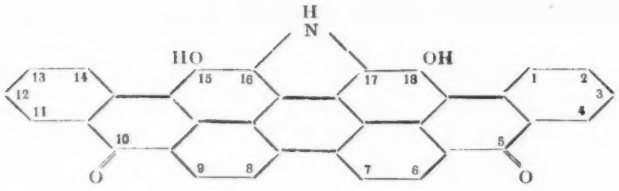
Received April 26, 1950

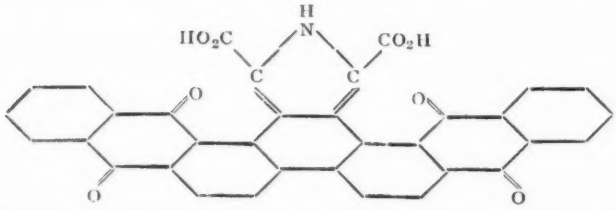
Nitration of dibenzanthrone with nitric acid in acetic acid, nitrobenzene or chloracetic acid (the last being used in one of the I. G. processes)[1] at 20–35° gives a mixture of mono- and dinitrodibenzanthrone, dyeing an unlevel green (Indanthrene Green B) of no practical value.[2] Since the nitro groups are reduced during vatting, the product on the fibre is a mixture of aminodibenzanthrones. When the green dye is oxidized on the fibre with hypochlorite (about 0·5% available chlorine) at room temperature, a deep fast black is produced.[3] Nitrodibenzanthrone is marketed under the name of Indanthrene Black B, BB, BGA, and is an important and largely used dye. Other examples of commercial nitrodibenzanthrones are Caledon Green BP and Caledon Black NB and 2B. The position of the nitro groups and the constitution of the black dye produced on the fibre are still undetermined. The nitrogen content (4·0%) of purified Caledon Black 2B indicates that it is approximately a 50% mixture of the mononitro and the dinitro derivatives (Calc. N, 2·8% and 5·1% respectively).

The available data on the constitution of dinitrodibenzanthrone, obtained by nitration of dibenzanthrone, is conflicting and inconclusive. Maki[4] considers that the nitro groups are in the 16: 17-positions, since the corresponding diamino compound, on oxidaton with chromic acid and sulphuric acid, gave first a brown alkali-soluble product (I) and ultimately a dicarboxylic acid (II); the proposed structures (I and II), however, were based mainly on nitrogen estimation. On the assumption of the 16: 17-orientation for the nitro groups, Maki concludes that the black dye, produced by hypochlorite oxidation of the diamine on the fibre, is the pyridazine derivative (III). Bennett, Pritchard and Simonsen[5] have obtained a carboxylic acid containing nitrogen by the chromic acid oxidation of dinitrodibenzanthrone, and this rules out the 16: 17-orientation since the oxidation of benzanthrone leads to anthraquinone-1-carboxylic acid. By analogy with other substitution reactions in the benzanthrone series, they regard dinitrodibenzanthrone as the 3: 12-compound. Oxidation gave a dinitro-

* Parts I and II of the Series have appeared as 'Anthraquinone Series, Parts I and II' in the *Proc. Ind. Acad. Sci.*, 1947, **25 A**, 467 and 1948, **28 A**, 236, respectively.

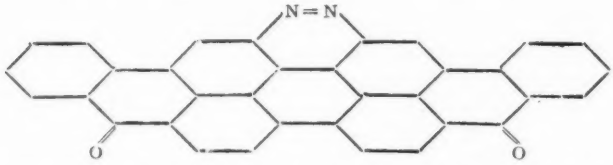


(I)



(II)

dianthraquinonyldicarboxylic acid, which on reduction and deamination *via* the diazonium salt gave 2:2′-dianthraquinonyl-1:1′-dicarboxylic acid, identical with the product of the oxidation of dibenzanthrone itself. We have now synthesized authentic 3:12-diaminodibenzanthrone (IV) by two routes, and found that it is different from the reduction product of dinitrodibenzanthrone. Dehalogenation of 3-bromo-9-aminobenzanthrone by



(III)

treatment with palladium and hydrazine hydrate[6] gave a mixture of the hitherto difficultly accessible 9-aminobenzanthrone as the major product, together with a small quantity of a vat dye which analysed for diaminodibenzanthrone and is obviously the 3:12-compound (IV).[7] The possibility of isodibenzanthrone formation during this dehalogenation is discounted by the fact that Busch and others[6] have noticed exclusive dibenzanthrone formation in such dehalogenations. The constitution (IV) for the new diaminodibenzanthrone was also confirmed by its unambiguous synthesis from 9:9′-dinitro-3:3′-dibenzanthronyl (VI) described later.

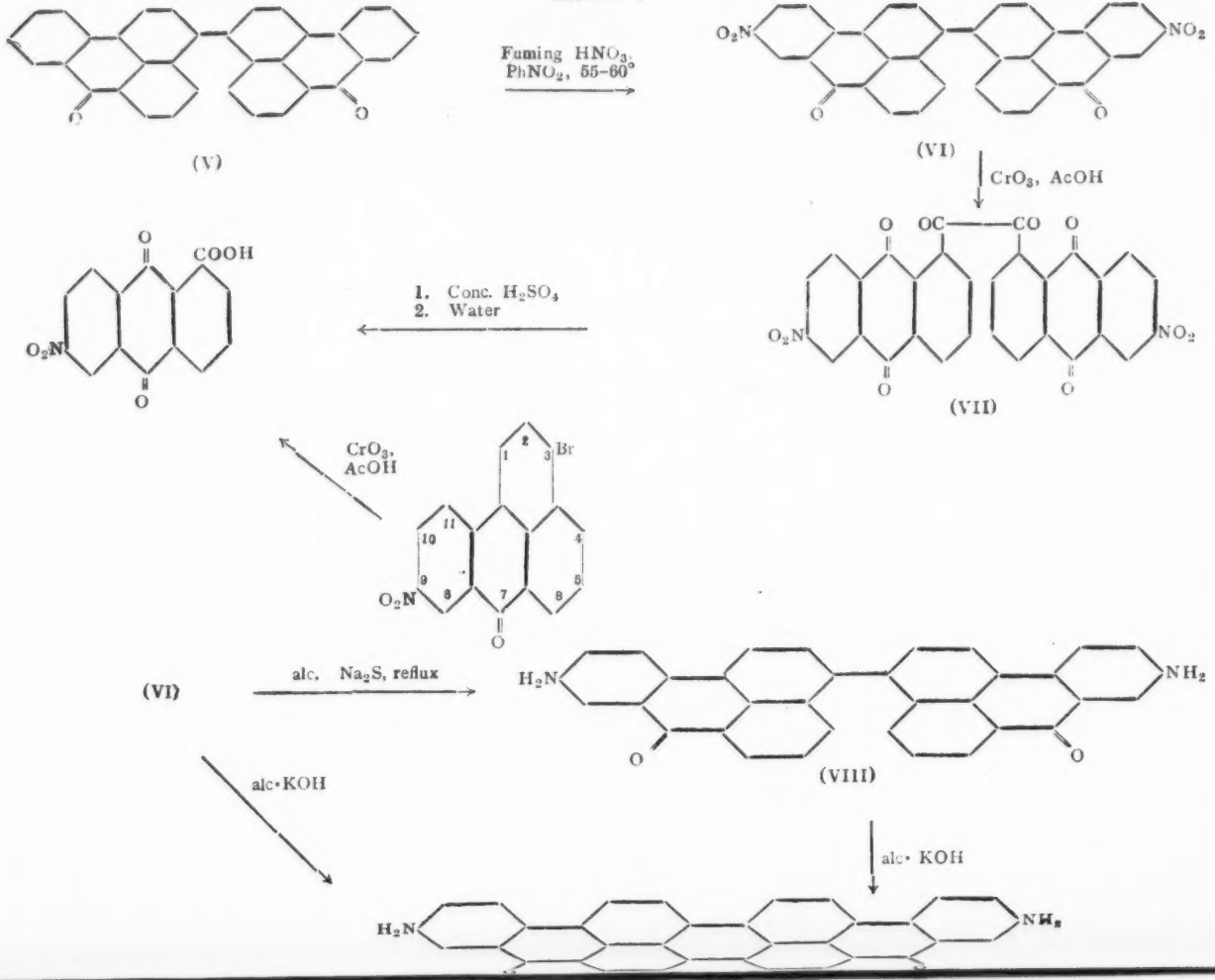
Dibenzanthrone, which forms the essential tinctorial constituent of the important vat dye Indanthrene Dark Blue BO (Bally, 1904; Colour Index No. 1099) (Caledon Dark Blue BM),[8] is prepared technically by the alkali fusion of benzanthrone, and it is somewhat difficult to isolate in pure form from the commercial product. One of the methods of obtaining pure

dibenzanthrone is the mild alkali fusion of 3:3′-dibenzanthronyl (V), which is obtained in good yield by the action of manganese dioxide and concentrated sulphuric acid on benzanthrone.[9] 3:3′-Dibenzanthronyl (V) can be readily isolated and crystallized from nitrobenzene, and it is of considerable interest as a starting material for the synthesis of dibenzanthrone derivatives of definite structure; but the orientation of substituents in 3:3′-dibenzanthronyl and the preparation of vat dyes from derivatives of (V) do not appear to have been studied.

Since in general the first substitution in benzanthrone takes place in the 3-position and subsequent substitution in the 9-position, it was anticipated that 3:3′-dibenzanthronyl (V), which can be regarded as a 3-substituted benzanthrone, would be attacked in the 9:9′-positions. Dinitration of (V) gave in fact the 9:9′-derivative (VI), the orientation of the nitro groups being established by oxidative degradation of (VI) to 6-nitroanthraquinone-1-carboxylic acid (see Chart 1).

Nitration of 3:3′-dibenzanthronyl to a dinitro-3:3′-dibenzanthronyl has been claimed in the patent literature,[10] but it has not been possible to obtain a homogeneous dinitro derivative under the conditions described. Nitration by means of concentrated nitric acid for 12 hours, according to the method of Maki[4] for dinitrodibenzanthrone, likewise gave an intractable mixture. A homogeneous dinitro-3:3′-dibenzanthronyl (VI) was finally obtained in good yield by the addition of fuming nitric acid (*d.*, 1·55) to a suspension of 3:3′-dibenzanthronyl in nitrobenzene. When (VI) was finely divided by precipitaton from sulphuric acid solution and then oxidized by means of chromic anhydride in boiling acetic acid, a light yellow crystalline powder, m.p. 420° (decomp.), was obtained, which analysed for dinitrodianthraquinonylglyoxal (VII). The glyoxal (VII) could not be converted into a nitroanthraquinone-carboxylic acid by the methods which are successful for dianthraquinonyl-1:1′-glyoxal and its 4:4′-dichloro derivatives;[11] hydrolysis with alcoholic sodium ethoxide gave a red product which was soluble in alkali, but not identifiable as a nitroanthraquinonecarboxylic acid. Fission by means of dimethyl sulphate was also unsuccessful. It was then found that concentrated sulphuric acid, in which (VII) does not dissolve initially, gradually dissolves it with the formation of a deep red solution, from which 6-nitroanthraquinone-1-carboxylic acid, m.p. 276–77°, identical with the product of oxidation of 3-bromo-9-nitrobenzanthrone with chromic acid in acetic acid,[12] was isolated. The dinitroglyoxal is, therefore, constituted as 6:6′-dinitrodianthraquinonyl-1:1′-glyoxal (VII), and the dinitrodibenzanthronyl obtained by the nitration of 3:3′-dibenzanthronyl as the 9:9′-dinitro derivative (VI).

CHART 1


Fuming HNO_3, $PhNO_2$, 55–60°
(V)
(VI)
CrO_3, AcOH
(VII)
1. Conc. H_2SO_4
2. Water
CrO_3, AcOH
alc. Na_2S, reflux
(VI)
(VIII)
alc·KOH
alc· KOH

Cyclization of 9 : 9′-dinitro-3 : 3′-dibenzanthronyl with alcoholic potassium hydroxide gave a diaminodibenzanthrone which is unambiguously constituted as 3 : 12-diaminodibenzanthrone (IV) and is identical with the dye obtained by the dehalogenation of 3-bromo-9-aminobenzanthrone described later.[7] While the green shade from nitrated dibenzanthrone, such as Indanthrene Black B, changes to a full black by hypochlorite oxidation, (IV) gave a dull green shade on cotton, which changed to blue by treatment with hypochlorite. Thus, the nitration of dibenzanthrone does not yield the 3 : 12-dinitro compound as suggested by Bennett, Pritchard and Simonsen.

The dinitrodibenzanthronyl (VI) gave 9 : 9′-diamino-3 : 3′-dibenzanthronyl (VIII) by reduction with alcoholic sodium sulphide; the diamine crystallized readily from quinoline and was characterized as its acetyl and benzoyl derivatives.

Chlorination of 3 : 3′-dibenzanthronyl with gaseous chlorine in boiling trichlorobenzene and chlorination by means of antimony pentachloride in nitrobenzene gave mixtures of products. A homogeneous dichloro derivative (IX), m.p. 420°, was obtained by passing chlorine through a suspension of the dinitro derivative (VI) in trichlorobenzene at 220° till a clear solution resulted. The chlorine atoms in (IX) are in the 9 : 9′-positions as proved by the oxidative degradation of (IX) to 6-chloroanthraquinone-1-carboxylic acid (XI) through the intermediate 6 : 6′-dichlorodianthraquinonyl-1 : 1′-glyoxal (X) (see Chart 2).

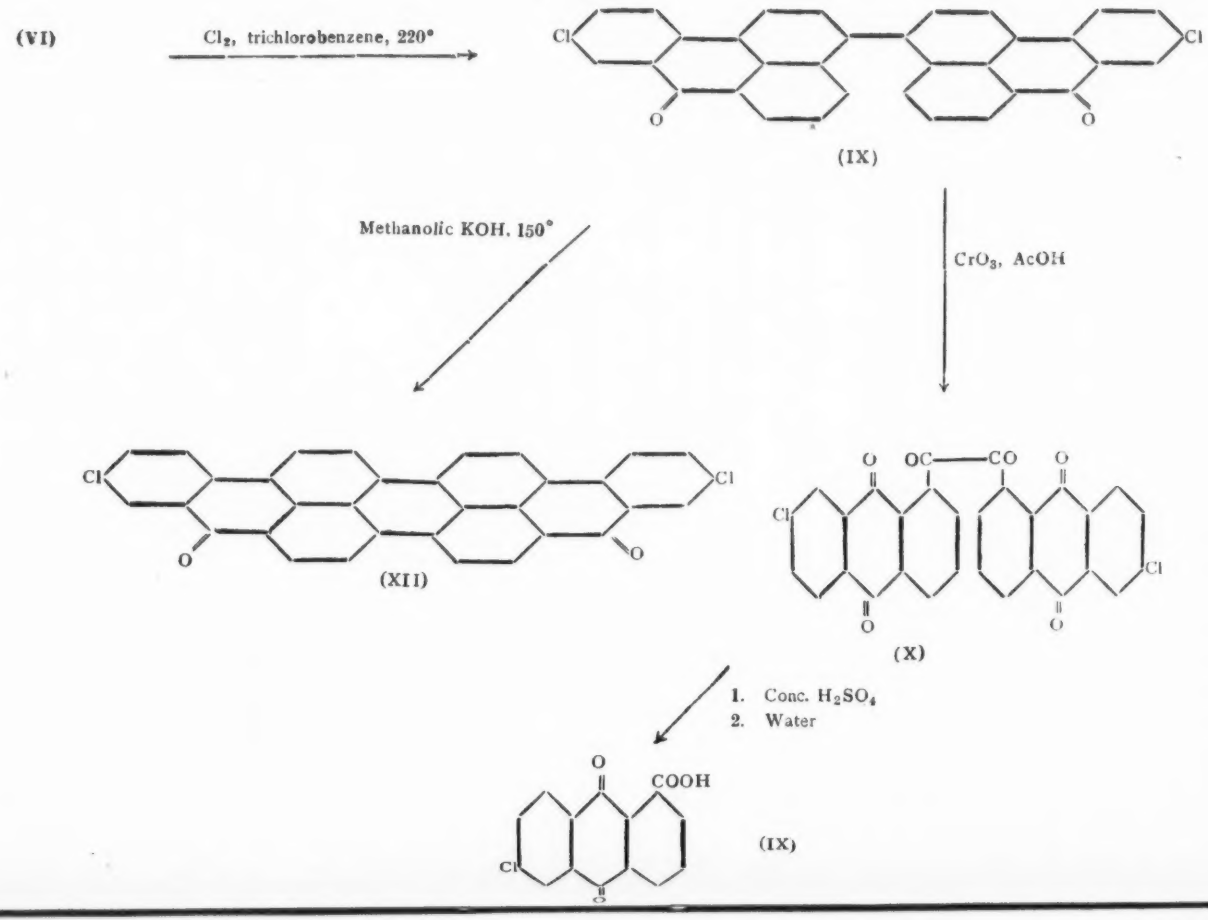
When 9 : 9′-dichloro-3 : 3′-dibenzanthronyl (IX) was heated in a sealed tube with methanolic caustic potash, the product was 3 : 12-dichlorodibenzanthrone (XII); dimethoxydibenzanthronyl and the corresponding dimethoxydibenzanthrone were not isolated.[13]

Experimental

9 : 9′-*Dinitro*-3 : 3′-*dibenzanthronyl* (*VI*)

3 : 3′-Dibenzanthronyl (V) (30 g.) was suspended in dry nitrobenzene (300 c.c.), nitric acid (*d.*, 1·55; 30 c.c.) added in the course of 30 minutes under stirring at 55–60°, and the mixture further stirred at this temperature for one and a half hours. After the addition of half the quantity of nitric acid, the suspended dibenzanthronyl went into solution, and as the reaction continued the nitro derivative gradually separated. It was collected, washed successively with nitrobenzene and benzene, and dried (22 g.). The nitro derivative crystallized from a large volume of nitrobenzene in shining minute orange-yellow needles which did not melt up to 550°. (Found: C, 74·2; H, 3·0; N, 5·1. $C_{34}H_{16}N_2O_6$ requires C, 74·4; H, 2·9; N, 5·1%.)

CHART II


(VI)
Cl_2, trichlorobenzene, 220°
Cl
O
O
Cl
(IX)
Methanolic KOH, 150°
CrO_3, AcOH
Cl
Cl
O
O
(XII)
O
OC—CO
O
Cl
Cl
O
O
(X)
1. Conc. H_2SO_4
2. Water
O
COOH
Cl
O
(IX)

6: 6′-*Dinitrodianthraquinonyl*-1 : 1′-*glyoxal* (*VII*)

The dinitro derivative (VI) (0·5 g.) was dissolved in concentrated sulphuric acid and reprecipitated with water. After washing the finely divided product free from sulphuric acid, it was washed with acetic acid and treated in boiling glacial acetic acid (25 c.c.) under reflux with chromic acid (4 g.) in the course of four hours. Refluxing was continued for two hours longer and the reaction mixture filtered hot. The residue was washed with acetic acid and water; the glistening mass of light yellow needles (0·25 g.) was crystallizable from nitrobenzene and trichlorobenzene, but the yield in the recrystallizations was poor. The crystalline reaction product itself, however, melted sharply at 420° (decomp.) and analysed for dinitrodianthraquinonyl-1: 1′-glyoxal (VII). (Found: C, 64·2; H, 2·1; N, 5·2. $C_{30}H_{12}N_2O_{10}$ requires C, 64·2; H, 2·4; N, 5·2%.) The product (VII) darkens in colour on exposure to air.

6-*Nitroanthraquinone*-1-*carboxylic acid*

The glyoxal (VII) (0·1 g.) was suspended in concentrated sulphuric acid (2 c.c.). In the course of one hour a dark red solution was obtained which on dilution with ice gave a greenish coloured product (0·1 g.), m.p. 255–60°. The latter gave a red solution in dilute aqueous ammonia and caustic soda, and the alkali solution on acidification gave the parent substance as a light yellow precipitate. The purified product on recrystallizing twice from dilute acetic acid was obtained as pale yellow needles, m.p. 276–77°, alone or admixed with authentic 6-nitroanthraquinone-1-carboxylic acid, m.p. 277–78°, prepared by oxidation of 3-bromo-9-nitrobenzanthrone with chromic acid in acetic acid.

3: 12-*Diaminodibenzanthrone* (IV)

A mixture of crystalline dinitrodibenzanthronyl (VI) (1 g.), caustic potash (8 g.) and methyl alcohol (15 c.c.) was heated to 120° under vigorous stirring for 2 hours, during which it darkened in colour. On dilution with water a red-violet solution of the reduced vat dye was obtained. The dye was recovered by aeration, filtered, washed with water and dried (0·9 g.). It was purified by vatting, filtering and reoxidizing when a green flocculent precipitate separated. Crystallization from quinoline gave a blue substance. (Found: C, 83·5; H, 4·0; N, 5·2. $C_{34}H_{18}N_2O_2$ requires C, 83·9; H, 3·7; N, 5·7%.) It dyes from a violet vat a dull green shade which turns to bright blue on hypochlorite oxidation.

9: 9′-*Diamino*-3: 3′-*dibenzanthronyl* (*VIII*)

Finely powdered dinitrodibenzanthronyl (VI) (4·16 g.) was refluxed under stirring with 10% alcoholic sodium sulphide (110 c.c.) for four hours.

The reaction mixture, which turned deep red in colour, was filtered, and the residue washed with hot water and alcohol and dried (3·7 g.). The diamine (VIII) crystallized from quinoline (280 c.c.) in brownish red needles (3 g.), which did not melt up to 550°. (Found: C, 83·9; H, 4·2; N, 5·4. $C_{34}H_{20}N_2O_2$ requires C, 83·6; H, 4·1; N, 5·7%.) The substance gives a red solution with concentrated sulphuric acid from which a yellow coloured sulphate separates on dilution with water.

9 : 9′-*Bis-acetamido*-3 : 3′-*dibenzanthronyl*

The crystallized diamine (VIII) (0·2 g.) was refluxed with glacial acetic acid (10 c.c.), acetic anhydride (10 c.c.) and 3 drops of pyridine for two hours. After cooling, the reaction mixture was filtered, and the residue washed with acetic acid and water. The scarlet product (0·23 g.) on crystallization from quinoline (50 c.c.) gave the diacetyl derivative as small disc-shaped crystals. (Found: N, 5·1. $C_{38}H_{24}N_2O_4$ requires N, 4·9%.)

9 : 9′-*Bis-benzamido*-3 : 3′-*dibenzanthronyl*

The diamine (VIII) (0·4 g.) was refluxed with benzoyl chloride (15 c.c.) for one hour, during which the colour of the reaction mixture changed from brownish red to yellow. After pouring in ice-water (600 c.c.), the mixture was left overnight, and the benzoyl derivative was washed with dilute ammonia and water, dried and crystallized from nitrobenzene (150 c.c.) when minute yellow needles were obtained. (Found: N, 3·9. $C_{48}H_{28}N_2O_4$ requires N, 4·0%.)

9 : 9′-*Dichloro*-3 : 3′-*dibenzanthronyl* (*IX*)

Dinitrodibenzanthronyl (VI) (0·5 g.) was suspended in trichlorobenzene (40 c.c.) kept at 220° by heating in an oil-bath, and dry chlorine gas was passed through the suspension for one hour. The dinitro derivative (VI), which was initially undissolved, went into solution at the end of the reaction. After removal of trichlorobenzene by steam distillation, a nitrogen-free chloro-compound (0·48 g.), m.p. 410–18°, was obtained. Two crystallizations from nitrobenzene gave yellow plates, m.p. 420–22°. (Found: C, 77·0; H, 3·1; Cl, 14·1. $C_{34}H_{16}Cl_2O_2$ requires C, 77·4; H, 3·1; Cl, 13·5%.)

3 : 12-*Dichlorodibenzanthrone* (*XII*)

The dichlorodibenzanthronyl (XI) (0·5 g.) was obtained in a finely divided form by precipitation from sulphuric acid solution, and after washing with water and methanol was suspended in methanolic potassium hydroxide (7 g. in 50 c.c.). The suspension was heated in a sealed tube for 7 hours at 150°.

The red reaction mixture was poured into water (400 c.c.), the suspension boiled and the precipitate collected (0·47 g.). The greyish blue product was sparingly soluble in boiling nitrobenzene, from which it crystallized in minute greyish blue needles. (Found: Cl, 13·4. $C_{34}H_{14}Cl_2O_2$ requires Cl, 13·5%.)

6:6′-*Dichlorodianthraquinonyl*-1:1′-*glyoxal* (*X*)

9:9′-Dichloro-3:3′-dibenzanthronyl (IX) (0·5 g.) was refluxed with glacial acetic acid (25 c.c.), and chromic anhydride (4 g.) was added in five lots during three hours. After refluxing for two hours, the mixture was filtered hot, washed with acetic acid and then with water. The residue (0·23 g.) was a light yellow crystalline powder, m.p. 310° (decomp.). (Found: Cl, 12·8. $C_{30}H_{12}Cl_2O_6$ requires Cl, 13·1%.)

6-*Chloroanthraquinone*-1-*carboxylic acid from* (*IX*)

The compound (IX) (0·1 g.) was treated with concentrated sulphuric acid (3 c.c.) when it dissolved with a red colouration. After leaving overnight the solution was poured into water, when a green precipitate separated (0·1 g.), m.p. 280–90°. It dissolved in alkali with a light red colouration and a light yellow substance (0·06 g.) precipitated on acidification. Two crystallizations from dilute acetic acid gave light yellow needles, m.p. 305-06°. The mixed m.p. with authentic 6-chloroanthraquinone-1-carboxylic acid was unaltered; Maki records the m.p. 307–08° (corr.).[14]

Summary

The orientation of the nitro groups in dinitrodibenzanthrone produced by nitration of dibenzanthrone has not been established so far. The suggestion of Simonsen *et al.*[5] that the nitro groups are in the 3:12-positions has been disproved by the unambiguous synthesis of 3:12-diaminodibenzanthrone (IV), which was found to be different from the diamino derivative obtained by the reduction of the above dinitrodibenzanthrone. The diaminodibenzanthrone (IV) was synthesized from 3:3′-dibenzanthronyl (V) by nitration to 9:9′-dinitro-3:3′-dibenzanthronyl (VI) and conversion of the latter in one step to (IV). The 9:9′-orientation of the nitro groups in (VI) was shown by its oxidation to 6-nitroanthraquinone-1-carboxylic acid.

Derivatives of 3:3′-dibenzanthronyl of definite orientation are useful as intermediates for the corresponding dibenzanthrone derivatives. Thus the dinitrodibenzanthronyl (VI) has been converted to 3:12-dichloro- and 3:12-diaminodibenzanthrone.

We are indebted to the Council of Scientific and Industrial Research under whose auspices this work was carried out, to Imperial Chemical

Industries (Dyestuff Group) for gifts of chemicals, and to Mr. T. S. Gore for the microanalyses recorded in the paper.

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ANTHRAQUINONE AND ANTHRONE SERIES

Part IV. Constitution of a Benzanthronequinoline and of Cyananthrene

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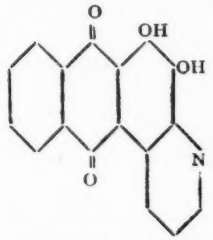
(Department of Chemical Technology, University of Bombay)

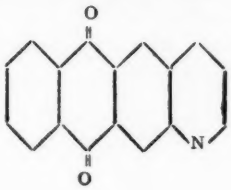
Received April 26, 1950

Prud'homme (1877) observed that the action of concentrated sulphuric acid on glycerine solutions of alizarin and nitroalizarin, prepared for calico printing, gave a blue dye with mordant dyeing as well as weakly basic properties. Brunck (1881) prepared the dye, Alizarin Blue (Colour Index No. 1066), in pure form and Graebe elucidated its constitution as a pyridine derivative (I) and the probable mechanism of the reaction. The Skraup synthesis of quinoline from aniline, nitrobenzene, glycerol and concentrated sulphuric acid was developed from this reaction. Alizarin Blue (I) is now prepared by heating a mixture of 3-nitro and 3-aminoalizarin with glycerol and 83% sulphuric acid at 110° for 3 hours. Expecting to produce a pyridinoanthraquinone (*e.g.*, II), Bally[1] treated 2-aminoanthraquinone with glycerol

(I)

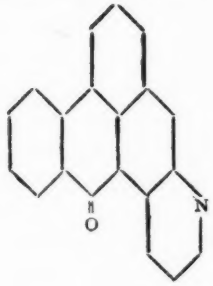


(II)

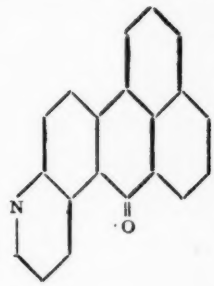


and sulphuric acid in the absence of an oxidising agent, and he obtained as the major product a compound $C_{20}H_{11}NO$, m.p. 251-52°, which was named benzanthronequinoline (III) or (IV); this name is used in the

(III)



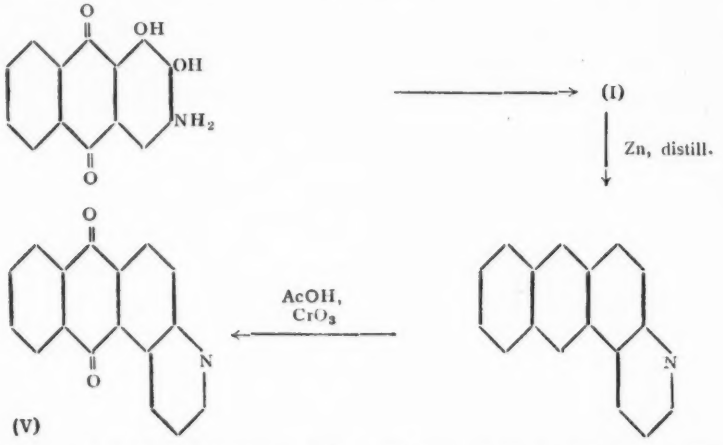
(IV)



present paper for Bally's compound, m.p. 251-52°. The anthraquinonequinoline (II), different from Graebe's angular isomer (V) (see later), was also isolated in low yield.

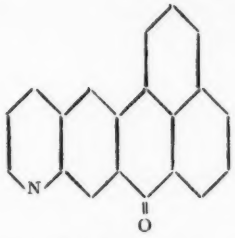
It was later shown by Bally[1] that anthraquinone itself, when treated with glycerol and sulphuric acid in the presence of a reducing agent, gave *meso*-benzanthrone, which forms the starting material for some of the fastest vat dyes. Alkali fusion of benzanthronequinoline gave a dipyridinodibenzanthrone, formerly marketed as Cyananthrene (Indanthrene Dark Blue BT; Bally, 1904; Colour Index No. 1117).[1, 2]

Benzanthronequinoline can also be produced by the further action of glycerine and sulphuric acid on 1 : 2 (*N*)-pyridinoanthraquinone (V). Benzanthronequinoline can thus be regarded as derived from (V) by the fusion of an additional benzene ring. The angular structure of (V) was proved by Graebe[3] by the following series of reactions.



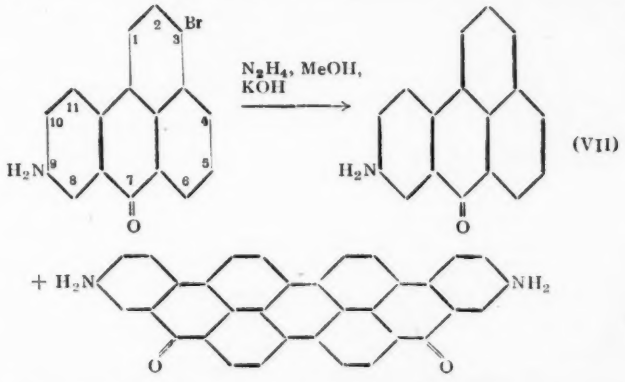
(V)

While the mode of attachment of the pyridine ring to the benzanthrone nucleus in benzanthronequinoline is thus known, the relative positions of the benzene and pyridine rings have not been established so far, and the compound has been represented both as (III) and (IV) in the literature.[1, 4] The constitution of benzanthronequinoline has now been proved to be (IV) by a Skraup synthesis from 9-aminobenzanthrone. A patent claim for the synthesis of benzanthronequinoline (IV) and the isomer (VI), m.p. 300°, starting from 9-aminobenzanthrone (VII), has been made, but the method by which the latter compound was prepared is not mentioned in the patent.[5]



(VI)

9-Aminobenzanthrone (VII) has been described by Copp and Simonsen,[6] who obtained it in low yield by a lengthy synthesis. It has now been prepared in three steps starting from 3-bromobenzanthrone. Nitration of the latter compound gave 3-bromo-9-nitrobenzanthrone, which on reduction with sodium sulphide in alcohol gave 3-bromo-9-aminobenzanthrone, m.p. 273-74°. Attempts to dehalogenate the bromonitrobenzanthrone by zinc and acetic acid gave the acetyl derivative of the corresponding amine. Dehalogenation by fusion with copper bronze was likewise unsuccessful. 9-Aminobenzanthrone (VII) was finally prepared by treatment of 3-bromo-9-aminobenzanthrone with palladium on calcium carbonate activated by hydrazine hydrate in methanolic caustic potash according to the method of Busch, Weber and Zink.[7] The desired 9-aminobenzanthrone was accompanied by a vat dye which crystallised in needles from quinoline, analysed for diaminodibenzanthrone, and is undoubtedly 3:12-diaminodibenzanthrone (VIII).



(VII)

(VIII)

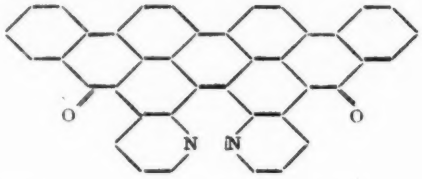
The constitution (VIII) assigned to this diaminodibenzanthrone was confirmed by its identity with 3:12-diaminodibenzanthrone prepared from 9:9′-dinitro-3:3′-dibenzanthronyl.[8] Busch and others[7] have recorded exclusive dibenzanthrone formation in the dehalogenation of 3-bromobenzanthrone by palladium and hydrazine. The dye (VIII) formed a red

vat and dyed cotton a dull green shade which changed to blue on oxidation with sodium hypochlorite solution.

9-Aminobenzanthrone (VII), on treatment with glycerine and sulphuric acid, yielded a pyridinobenzanthrone which was identical with benzanthronequinoline in all respects. Since the pyridine ring in the latter has been shown earlier to be fused to the anthrone nucleus in the angular position, the pyridino derivative obtained from 9-aminobenzanthrone (VII) and benzanthronequinoline obtained from 2-aminoanthraquinone are, therefore, constituted as (IV).

Maki and Aoyoma[9] prepared a bromobenzanthronequinoline from 2-bromo-3-aminoanthraquinone by treatment with glycerine and sulphuric acid. Fusion of this bromobenzanthronequinoline with caustic potash gave a dihydroxy derivative of cyananthrene, and not cyananthrene. Maki and Aoyama[9] then inferred that benzanthronequinoline was constituted as (IV).

Bally, who discovered benzanthronequinoline and cyananthrene, did not decide between alternative structures for them. Schultz[2] assigns the alternative structure (IX) to cyananthrene. The fact that benzanthronequinoline has now been proved to be (IV) gives experimental support to the constitution (X) assigned to cyananthrene in the Colour Index.



(IX)

(X)

Experimental

Benzanthronequinoline (IV).—β-Aminoanthraquinone (18 g.) was dissolved in concentrated sulphuric acid (130 c.c.) and the solution was diluted with water (15 c.c.) under stirring at room temperature. Glycerine (18 g.) and water (15 c.c.) were then added gradually during 30 minutes at 50°. The temperature was raised slowly during 1½ hr. to 155° and the reaction mixture maintained at this temperature for 2 hours. On cooling to 70°, and pouring into water (600 c.c.) at 70°, the yellow product was

filtered, washed free from acid, extracted with 1% caustic soda solution, washed with water and dried (24 g.). The product melted at about 220°. Crystallization from xylene gave yellow needles (11·5 g.), but the m.p. was not raised. The crystalline substance, after washing with warm 25% sulphuric acid and water, was recrystallized from a large volume of xylene, when benzanthronequinoline separated as clusters of elongated needles, m.p. 251-52° (Found: C, 85·4; H, 3·8; N, 5·1. $C_{20}H_{11}NO$ requires C, 85·4; H, 3·9; N, 5·1%). The substances accompanying benzanthronequinoline in this reaction will be reported upon later. It was observed in some experiments that the reaction mass set to a solid after half the amount of aqueous glycerine had been added at 50°; on raising the temperature and adding the remainder of the glycerine the mass liquefied again. Under these conditions benzanthronequinoline was produced in maximum yield (9 g. from 18 g. of β-aminoanthraquinone) and was readily isolable by working up the reaction product as described earlier and crystallization from xylene.

3-*Bromo*-9-*aminobenzanthrone*.—3-Bromo-9-nitrobenzanthrone was prepared according to Day[10] by the nitration of 3-bromobenzanthrone (30 g.) in nitrobenzene (150 g.) with 98% nitric acid (25 g.). The bromonitro derivative (30 g.) was obtained in a finely divided form by dissolving in concentrated sulphuric acid and reprecipitating with water. After washing the product free from acid, it was suspended in alcohol (450 c.c.) and an aqueous solution of fused sodium sulphide (60 g.) in water (150 c.c.) was then added. The mixture was refluxed for 3 hours under stirring and filtered hot. The residue was washed with hot water and dried (21 g.; m.p. 270-72°). After crystallization from *o*-dichlorobenzene the lustrous dark red needles of 3-bromo-9-aminobenzanthrone had m.p. 273-74°. (Found: Br, 24·3; N, 4·5. $C_{17}H_{20}BrNO$ requires Br, 24·7; N, 4·3%.)

The amine dissolved in sulphuric acid with a dark red colour; careful dilution with water precipitated the yellow sulphate. In azoic dyeing the diazotized amine gave orange, purple and reddish brown shades on yarn impregnated with Brenthol AT (Naphtol AS-G), Brenthol AS and Naphtol AS-GR respectively.

3-*Bromo*-9-*acetamidobenzanthrone*.—The above amine (0·5 g.) was refluxed with acetic anhydride (15 c.c.) for 30 minutes and the product which separated on cooling was crystallized from nitrobenzene. The orange-yellow needles melted at 304-05° (Found: Br, 21·6; N, 3·8. $C_{19}H_{12}BrNO_2$ requires Br, 21·8; N, 3·7%.)

3-*Bromo-9-benzamidobenzanthrone*.—The amine (1 g.) was refluxed with benzoyl chloride (0·6 g.) in nitrobenzene (19 g.) for 2 hours. On cooling, orange-yellow needles separated. After two recrystallizations from nitrobenzene, the m.p. was 278-79°. (Found: Br, 18·5; N, 3·8. $C_{24}H_{14}BrNO_2$ requires Br, 18·7; N, 3·2%.)

9-*Aminobenzanthrone* (*VII*).—3-Bromo-9-aminobenzanthrone (1·27 g.) was mixed with palladium—calcium carbonate catalyst (1 g.) containing 1% palladium and heated in a sealed tube at 140-45° with acetone-free methanol (25 c.c.), caustic potash (2·5 g.) and hydrazine hydrate (85% solution; 0·6 c.c.) for 1½ hours. After acidifying with hydrochloric acid, boiling and filtering, the yellow solution was neutralized. A bright red substance (0·75 g.), which contained no bromine and had m.p. 218-22° separated. It crystallized from chlorobenzene in bright, deep red needles, m.p. 225-26°. (Found: C, 83·2; H, 4·8; N, 5·6. $C_{17}H_{11}NO$ requires C, 83·2; H, 4·5; N, 5·7%.) Copp and Simonsen[6] quote m.p. 216-17°. The residue (0·23 g.), insoluble in dilute hydrochloric acid was a bluish substance containing no bromine and dyeing cotton from a violet vat a dull green shade which changed to bright blue after hypochlorite oxidation. The dye crystallized from quinoline in blue needles. (Found: C, 83·5; H, 4·0; N, 5·2. $C_{34}H_{18}N_2O_2$ requires C, 83·9; H, 3·7; N, 5·7%.)

9-*Acetamidobenzanthrone* crystallized from toluene in shining yellow plates, m.p. 228-30°. (Found: N, 4·6. $C_{19}H_{13}NO_2$ requires N, 4·8%.)

9-*Benzamidobenzanthrone*.—A solution of 9-aminobenzanthrone (0·1 g.) in warm benzoyl chloride (1 c.c.) was acidified with a drop of concentrated sulphuric acid, when a copious evolution of hydrogen chloride took place and the colour of the solution changed to deep red. After leaving for 15 minutes the reaction mixture, which had solidified, was drowned in ice-water. The precipitate that separated was washed with sodium carbonate solution, then with water and dried. Crystallization from *o*-dichlorobenzene gave brown dumb-bell shaped crystals, m.p. 248-49°. (Found: N, 3·9. $C_{24}H_{16}NO_2$ requires N, 4·0%.)

Benzanthronequinoline (*IV*) *from* 9-*aminobenzanthrone* (*VII*).—9-Aminobenzanthrone (VII) (0·3 g.) was dissolved in concentrated sulphuric acid (3·3 c.c.), and a solution of glycerine (0·3 g.) in water (1 c.c.) was gradually added under stirring at 100° during one hour. After further heating at 145–50° for 4 hours, the reaction mixture was cooled and poured into ice-water (200 c.c.). The yellow substance which separated was washed with water till free from acid, then boiled with 1% caustic soda solution, filtered, washed and dried. The dirty green product (0·4 g.) crystallized from xylene

(Norit) in brownish yellow crystals. Recrystallization from xylene gave bright yellow needles, m.p. 251-52°, undepressed when mixed with benzanthronequinoline, m.p. 251-52°, described earlier.

Summary

9-Aminobenzanthrone, which has been prepared earlier by a tedious synthesis, has now been prepared from 3-bromobenzanthrone by nitration to 3-bromo-9-nitrobenzanthrone, reduction of the nitro derivative to 3-bromo-9-aminobenzanthrone, and debromination of the latter compound by palladium and hydrazine. 3:12-Diaminodibenzanthrone (VIII) was formed as a minor product in the debromination.

While the angular orientation of the fused pyridine ring in benzanthronequinoline, a product obtained by the action of glycerine and sulphuric acid on 2-aminoanthraquinone, has been established, the relative positions of the benzene and pyridine rings has not been proved so far. The Skraup reaction on 9-aminobenzanthrone gave benzanthronequinoline, thus proving its constitution as (IV). Cyananthrene, a vat dye obtained by alkali fusion of benzanthronequinoline, is therefore constituted as (X), and not as (IX) as sometimes stated in the literature.

We are indebted to the Council of Scientific and Industrial Research for a fellowship awarded to one of us (P. N. P).

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THE RESOLUTION OF THE CLIFFORD ALGEBRA (DIRAC ALGEBRA) WITH ANY NUMBER OF SYMBOLS AS THE DIRECT SUM OF MINIMAL LEFT IDEALS

By K. N. Srinivasa Rao and C. K. Venkatanarasimhiah

Received February 10, 1950
(Communicated by Prof. B. S. Madhava Rao, F.A.SC.)

Introduction

In this note the Clifford-Dirac Algebra generated by n-symbols $e_1, e_2, \ldots e_n$ satisfying the relations

$$e_r e_s + e_s e_r = 2\delta_{rs} \text{ (Kronecker symbol)}$$

over a ground field whose characteristic $\neq 2$ and which contains $\sqrt{-1}$ is resolved into the sum of minimal left ideals. These ideals as well as their bases have been chosen in a suitable manner and the corresponding representation is seen to be identical with the well-known one given by Weyl and Brauer.[1]

We wish to thank Dr. K. Venkatachaliengar for suggesting the problem and helpful guidance, and Prof. B. S. Madhava Rao for kind encouragement.

§1. It is well known+ that the basis elements of the Clifford Algebra with the n symbols $e_1, e_2, \ldots e_n$ satisfying the relation

I. $e_r e_s + e_s e_r = 2\delta_{rs}$ (δ_{rs} Kronecker symbol) are all expressed succinctly by the expression $e_1^{\lambda_1}, e_2^{\lambda_2} \ldots e_n^{\lambda_n}$ where the $\lambda's$ are integres mod 2. Evidently there are 2^n basis elements.

We deduce easily,

II. (1) $e_1 e_2 \ldots e_{2r+1}$ commutes with the e_p; $p \leqslant 2r+1$
and
anticommutes with the e_p; $p > 2r+1$.

II. (2) $e_1 e_2 \ldots e_{2r}$ anticommutes with the e_p; $p \leqslant 2r$
and
commutes with the e_p; $p > 2r$.

II. (3) $(e_1e_2\ldots.e_{2r})^2 = (-1)^r$

II. (4) $(e_1e_2\ldots.e_{2r+1})^2 = (-1)^r$

It follows also that the algebra C_{2n+1} (generated by an odd number of symbols) can be resolved into a direct sum of two simple algebras each of which is isomorphic with a C_{2n}: *i.e.*,

$$C_{2n+1} = C_{2n+1}\omega + C_{2n+1}(1-\omega) \text{ where}$$

$$\omega = \frac{1 + e_1e_2\ldots.e_{2n+1}}{2} \text{ if } n \text{ is even or}$$

$$= \frac{1 + i\,e_1e_2\ldots.e_{2n+1}}{2} \text{ if } n \text{ is odd.}$$

§2. We now take up the complete resolution of a C_{2n} as a direct sum of minimal, mutually orthogonal left ideals. For this purpose we make use of a result due to Witt,[2] *viz.*, that a Clifford Algebra with $2n$ symbols is the direct product of n such algebras with 2 symbols. Witt has shown that

$$C_{2n} = (1, e_1, e_2) \times (1, ie_1e_2e_3, ie_1e_2e_4) \times (\ldots\ldots) \ldots\ldots \times (\qquad)$$

where each of the brackets represents an algebra generated by the symbols contained in it. Therefore, the idempotents generating minimal left ideals in C_{2n} are given by

$$\omega_r = \frac{(1 \pm e_1)}{2} \cdot \frac{(1 \pm ie_1e_2e_3)}{2}, \ldots. \frac{(1 \pm i^{k+1}e_1e_2\ldots.e_{2k-1})}{2} \ldots\ldots\ldots n$$

factors. Corresponding to the two signs $\pm$ in each of the brackets there are evidently 2^n such ω_r's. We now show that

$$\omega_r^2 = \omega_r \text{ and } \omega_r\omega_s = 0 \text{ if } r \neq s.$$

Now

$$\omega_r^2 = \left\{\frac{(1 \pm e_1)}{2} \ldots. \frac{(1 \pm i\,c_1e_2\ldots.e_{2n-1})}{2}\right\} \left\{\frac{(1 \pm e_1)}{2} \ldots. \frac{(1 \pm i\,e_1e_2\ldots.e_{2n-1})}{2}\right\} n \text{ even}$$

$$= \left(\frac{1 \pm e_1}{2}\right)^2 \ldots. \left(\frac{1 \pm i\,e_1e_2\ldots.e_{2n-1}}{2}\right)^2$$

$$= \frac{(1 \pm e_1)}{2} \ldots. \frac{(1 \pm i\,e_1e_2\ldots.e_{2n-1})}{2} = \omega_r$$

To show that $\omega_r\omega_s = 0\ (\gamma \neq s)$ we first observe that in the expressions for ω_r and ω_s, there is at least one bracket which appears with a change of sign in it. Calling this the pth bracket, if it is $\frac{(1 + i e_1e_2 \ldots e_{2p-1})}{2}$ in ω_r, it will be $\frac{1 - i e_1e_2 \ldots e_{2p-1}}{2}$ in ω_s. Since the factors in the brackets commute with one another, we can bring the pth brackets together in $\omega_r\omega_s$. But

$$\frac{(1 + i e_1e_2 \ldots e_{2p-1})}{2} \quad \frac{(1 - i e_1e_2 \ldots e_{2p-1})}{2} = 0$$

Hence $\omega_r\omega_s = 0$ if $r \neq s$.

We next prove that $\sum_{r=1}^{r=2^n} \omega_r = 1$.

Proof.—Let the result be true for $n = m$

$$i.e., \sum_{r=1}^{r=2^m} \omega_r = \sum_{1}^{2^m} \frac{(1 \pm e_1)}{2} \ldots \frac{(1 \pm i e_1e_2 \ldots e_{2m-1})}{2} = 1 \text{ for } C_{2m}$$

Hence for C_{2m+2},

$$\sum_{1}^{2^{m+1}} \omega_r = \sum_{1}^{2^{m+1}} \frac{(1 \pm e_1)}{2} \ldots \frac{(1 \pm i e_1 \ldots e_{2m-1})}{2} \frac{(1 \pm e_1e_2 \ldots e_{2m+1})}{2}$$

$$= \left(\sum_{1}^{2^m} \frac{(1 \pm e_1)}{2} \ldots \frac{(1 \pm i e_1 \ldots e_{2m-1})}{2}\right) \frac{(1 + e_1e_2 \ldots e_{2m+1})}{2}$$

$$+ \left(\sum_{1}^{2^m} \frac{(1 \pm e_1)}{2} \ldots \frac{(1 \pm i e_1 \ldots e_{2m-1})}{2}\right) \frac{(1 - e_1e_2 \ldots e_{2m+1})}{2}$$

$$= \frac{1 + e_1e_2 \ldots e_{2m+1}}{2} + \frac{1 - e_1e_2 \ldots e_{2m+1}}{2} = 1$$

i.e., the result is true for $n = m + 1$. But for $n = 1$,

$$\Sigma\, \omega_r = \Sigma \frac{1 \pm e_1}{2} = 1 \text{ and hence it is true for all } n.$$

We now proceed to deduce the irreducible representation of the algebra C_{2n} by choosing a suitable basis of the minimal left ideal L: generated by one of ω_r's, say

$$\omega = \frac{(1+e_1)}{2}\ \frac{(1+i\,e_1e_2e_3)}{2}\ \ldots\ \frac{(1+i\,e_1e_2\ldots e_{2k-1})}{2}\ \ldots\ \frac{(1+i\,e_1e_2\ldots e_{2n-1})}{2}$$

we first of all show that

$$e_{2k+1}\,\omega = (-1)^k\, i\, e_{2k}\,\omega \quad k = 1, 2, \ldots, n-1.$$

Proof.—(i) Let k be even: From II. 1.

$$e_{2k}\,\omega = e_{2k}\left(\frac{1+e_1}{2}\right)\ldots\left(\frac{1+i\,e_1e_2\ldots e_{2k-1}}{2}\right)\ldots\frac{(1+i\,e_1e_2\ldots e_{2n-1})}{2}$$

$$= \frac{(1-e_1)}{2}\ldots\left(\frac{1-i\,e_1e_2\ldots e_{2k-1}}{2}\right)\left(\frac{e_{2k}-e_1\ldots e_{2k-1}\,e_{2k+1}}{2}\right)\ldots\frac{(1+i\,e_1\ldots e_{2n-1})}{2}$$

$$e_{2k+1}\,\omega = \left(\frac{1-e_1}{2}\right)\ldots\left(\frac{1-i\,e_1\ldots e_{2k-1}}{2}\right)\left(\frac{e_{2k+1}+e_1\ldots e_{2k}}{2}\right)\ldots\left(\frac{1+i\,e_1\ldots e_{2n-1}}{2}\right)$$

$$= \left(\frac{1-e_1}{2}\right)\ldots\left(\frac{1-i\,e_1\ldots e_{2k-1}}{2}\right)[e_1\ldots e_{2k-1}]\times$$

$$\times\left(\frac{e_{2k}-e_1\ldots e_{2k-1}\,e_{2k+1}}{2}\right)\ldots\frac{(1+i\,e_1\ldots e_{2n-1})}{2}\ \text{using II. 4.}$$

$$= \left(\frac{1-e_1}{2}\right)\ldots\left(\frac{e_1\ldots e_{2k-1}+i}{2}\right)\left(\frac{e_{2k}-e_1\ldots e_{2k-1}\,e_{2k+1}}{2}\right)\ldots\left(\frac{1+i\,e_1\ldots e_{2n-1}}{2}\right)$$

$$= i\,e_{2k}\,\omega. \qquad (a)$$

(ii) Let k be odd.

$$e_{2k}\,\omega = \left(\frac{1-e_1}{2}\right)\ldots\left(\frac{1-e_1\ldots e_{2k-1}}{2}\right)\left(\frac{e_{2k}-i\,e_1\ldots e_{2k-1}\,e_{2k+1}}{2}\right)\ldots\left(\frac{1+i\,e_1\ldots e_{2n-1}}{2}\right)$$

$$e_{2k+1}\,\omega = \left(\frac{1-e_1}{2}\right)\ldots\left(\frac{1-e_1\ldots e_{2k-1}}{2}\right)\left(\frac{e_{2k+1}+i\,e_1\ldots e_{2k}}{2}\right)\ldots$$

$$\left(\frac{1+i\,e_1\ldots e_{2n-1}}{2}\right)$$

$$= \left(\frac{1-e_1}{2}\right)\ldots\left(\frac{1-e_1\ldots e_{2k-1}}{2}\right)[i\,e_1\ldots e_{2k-1}]\times$$

$$\times\left(\frac{e_{2k}-i\,e_1\ldots e_{2k-1}\,e_{2k+1}}{2}\right)\ldots\left(\frac{1+i\,e_1\ldots e_{2n-1}}{2}\right)$$

$$= \left(\frac{1-e_1}{2}\right)\ldots\left(\frac{i\,e_1\ldots e_{2k-1}-i}{2}\right)\left(\frac{e_{2k}-i\,e_1\ldots e_{2k-1}\,e_{2k+1}}{2}\right)$$

$$\ldots\left(\frac{1+i\,e_1\ldots e_{2n-1}}{2}\right)$$

$$= -\,i\,e_{2k}\,\omega. \qquad (b)$$

Combining (*a*) and (*b*) we get

$$e_{2k+1}\,\omega = (-1)^k\,i\,e_{2k}\,\omega.$$

We thus see that all the symbols with odd suffixes can be expressed in terms of those with even suffixes only and that $e_1\omega = \omega$. We therefore take, as the basis elements of the minimal left ideal generated by ω the 2^n terms occurring in

$$e_{2n}^{\lambda_n}\,e_{2n-2}^{\lambda_{n-1}}\ldots\,e_2^{\lambda_1}\omega = a_r\,\omega \text{ where the } \lambda\text{'s are integers mod.2.}$$

The e's are written down, as above, with the suffixes, always in the descending order and $\lambda_1, \lambda_2, \ldots, \lambda_n$ take the values 0, 1 in the dictionary order. Each a_r represents a particular combination of the e's and r takes 2^n values. We add a direct proof that the $a_r\,\omega$ are linearly independent.

Proof.—We first show that if a represents some combination of the e's, $a\omega_r = \omega_s a$ where ω_r and ω_s are two *different* mutually orthogonal idempotents. Now an a is of the form

$$a = e_{2l}\,e_{2m}\ldots e_{2s}e_{2t}, \text{ where } n \geqslant l > m \ldots > s > t \geqslant 1$$

Hence $a\omega_r = e_{2l}\,e_{2m}\ldots e_{2s}e_{2t}\omega_r$.

From II. 1, when e_{2t} is taken to the right of ω_r, one can see easily that there will be a change of sign in the first t brackets only. If now e_{2s} is brought

to the right of ω_r, the signs will be restored in the first t brackets, but a change of sign occurs in the next $s-t$ brackets and the last $n-s$ brackets remain unaltered. We thus observe that when all the e's are taken to the right of ω_r, it would have changed over to a different orthogonal idempotent ω_s,

$$i.e.,\ a\omega_r = \omega_s a \ (r \neq s)$$

Let now $\sum_{r=1}^{r=2^n} a(\alpha_r\omega) = 0$, *i.e.*,

$$a_1\alpha_1\omega + a_2\alpha_2\omega + \ldots + a_r\alpha_r\omega + \ldots + a_{2^n}\alpha_{2^n}\omega = 0$$

$$i.e.,\ a_1\omega_{s_1}\alpha_1 + a_2\omega_{s_2}\alpha_2 + \ldots + a_r\omega_{s_r}\alpha_r + \ldots + a_{2^n}\alpha_{s_{2^n}}\omega = 0$$

Multiply by ω_{sr} $(r = 1, 2, \ldots 2^n)$ on the left. We obtain

$$a_r\omega_{sr}{}^2\alpha = a_r\omega_{sr}\alpha_r = 0$$

$$i.e.,\ a_r = 0,\ (r = 1, 2, \ldots 2^n,)\ i.e.,\ \text{the } \alpha_r\omega \text{ are linearly independent.}$$

Choosing these as the basis elements of the left ideal L: generated by ω, we can obtain the matrices of the representation in terms of the Pauli matrices

$$P_1 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},\ P_2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ P_3 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \text{ and } E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The matrices are easily seen to be

$$e_1 \rightarrow P_1 \times P_1 \times P_1 \times \ldots\ldots \times P_1 \times P_1 \times P_1 \qquad n \text{ terms}$$

$$e_{2k} \rightarrow P_1 \times P_1 \times \ldots\ldots \times P_2 \times P \times E \times E \times \ldots\ldots \times E \qquad ,,$$

$$e_{2k+1} \rightarrow (-1)^k P_1 \times P_1 \times \ldots\ldots \times P_1 \times P_3 \times E \times \ldots\ldots \times E_1 \qquad ,,$$

where P_2 and P_3 occur in the kth place from the right end in the corresponding expressions.

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ARRHENIUS PARAMETERS AND CHEMICAL REACTIVITY

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Received May 19, 1950

1. Introduction

In a chemical reaction, the reactants represent one system of minimum potential energy and the products another one, also of minimum potential energy while the transition state is at a higher energy level than either of these. The energy required to raise the energy level of the reactants to that of the transition state may be considered to be the activation energy of the reaction. Though the original explanation of Arrhenius has to be modified, the rate of conversion can still be represented by the classical reaction rate equation:

$$k_r = \chi e^{-E/RT}$$

whether one approaches the problem from the collision hypothesis or the theory of absolute reaction rates. The principal difference in the two modes of approach is in the interpretation of the frequency factor. The collision theory associates the term with the number of "collisions" or encounters among the reactant molecules modified by a factor which takes into account other unknown conditions, with the result that the parameters can be computed only from experimental observations. The theory of absolute reaction rates on the other hand makes the term a composite one involving the term kT/h a universal frequency common to all reactants multiplied by the ratio of the partition functions. The two approaches lead to the same result only in the case of reactions between two atoms. A serious limitation to the theory is the application of equilibrium theory to systems which are certainly not at equlibrium and the difficulty in extending rigorous calculations to complex organic molecules, successive reactions and chain reactions. In spite of the theoretical limitations from either approach, however, it is useful to consider the parameters in the final analysis of reaction mechanisms and the problem of bond fixation. The present communication is a fuller analysis of this latter problem reported before (6) and the closely related problem of reactivity. Chemical reactions are such normal tools for an organic chemist that it is worth while examining the basis of the procedure.

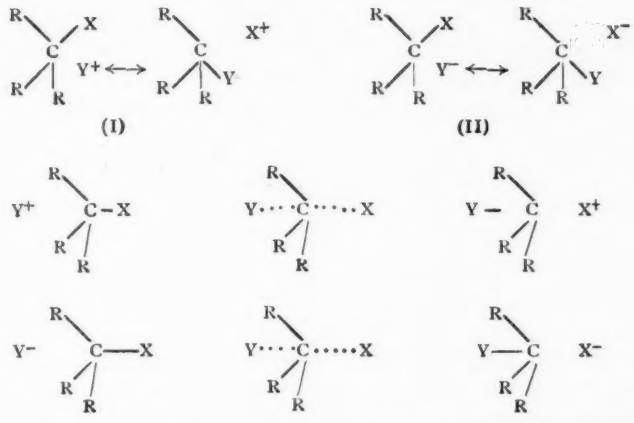
2. The Activation Energy of Homogeneous Organic Reactions

In the first instance, it will be convenient to confine our analysis to the case of homogeneous reactions alone. Even here, one has a large variety of reactions to consider which can be grouped as under in Table I.

TABLE I

Reagent initiating attack	Second Reactant	
	Aliphatic compounds	Aromatic compounds
1 Electrophilic ..	(*a*) Saturated system Substitution involving Walden Inversion	(*a*) Nuclear substitution
2 Nucleophilic ..	(*b*) Saturated system Substitution without Walden inversion	(*b*) Side chain substitution
3 Free radical ..	(*c*) Unsaturated systems	..

The influence of a substituent on the activation energy of a reaction will naturally vary with the nature of the reaction considered and any quantitative comparisons must necessarily be confined to those reactions in the same category. In the aliphatic series, free radical reactions may not be as varied as in the aromatic group but are nonetheless important and will be considered in a later section. Turning to the other two types, the transition state can in general be represented by the following scheme:



The transition states I and II correspond to systems where there is no Walden inversion during substitution while the latter two correspond to

systems involving Walden inversion, the two sets corresponding to the classifications $S_N 1$ and $S_N 2$ of Hughes and Ingold (15).

The calculation of the resonance energy of the transition state may not be feasible in most cases and in any case uncertain, but if one is studying a homologous series or the influence of substitution on a specific reaction, large variations in this may not be expected and changes in activation energy can be primarily attributed to changes in the state of polarisation of the molecule as a result of substitution. The introduction of an $\alpha\beta$ double bond can lead to a resonance hybrid structure involving this bond also in the transition state and add to the uncertainty of calculated values. If the resonance energy happens to be about the same as that required for the ionisation of the C-X bond, it is quite possible that the reaction leads to a first order velocity constant and the activation energy for the reaction is less than that required by a bimolecular mechanism. It will be shown in a later section how this picture fits in with the Hughes-Ingold mechanism of substitution at a saturated carbon atom.

The course of a reaction can be broadly pictured thus:

Reactant or Reactants $\leftrightarrows$ Energised molecule or molecules $\leftrightarrows$ Transition state $\leftrightarrows$ Products

Variations in the final analysis arise from the choice of the rate-determining step for the reaction in question. In a unimolecular reaction the third step is the slowest while in bimolecular mechanisms, the slowest step will be the formation of the activated molecules. Whatever the mechanism, for the reaction to take place, the energy must be essentially localised in the bond undergoing the transformation and changes in activation energy may be expected for corresponding changes in the bond energy. Available experimental data can now be analysed to see how far this picture is in conformity with facts.

In the aliphatic series, the only reactions where the reagent is electrophilic (Cationoid) are those involving halogenations and nitrations in the gas phase nitrations involve also breakdown of the higher homologues and results at present do not permit of proper analysis. Halogenations are also quite complex but the comprehensive investigations of Vaughan and coworkers (26) bring out a few salient features. Even though saturated hydrocarbons are nonpolar, it is now well recognised (9) that the C-H bond energy is different according as the carbon atom is primary, secondary or tertiary and this should be reflected in their reactivity. The reaction is one involving a chain mechanism and though neither rate constants nor activation energies are available, the yield of the different products with a

given rate of flow can serve for comparison. Of the two alternative formulations of the transition state, I and III, I requires that replacement of hydrogen by chlorine should be in the order primary, secondary, tertiary in the hydrocarbons but the introduction of one halogen in a hydrocarbon leads to further substitution in the same carbon atom as the carbon hydrogen bond has a reduced force constant (*vide* Linnett 18). This is seen to be the case from the observations of Rust and Vaughan (*loc. cit.*). It should be mentioned, however, that these figures refer to temperatures above 300° C. At lower temperatures, the proportions are different but the reaction also appears more complex.

TABLE II

Compouud chlorinated	Products
Propane ..	*n*-Propyl Chloride 43% iso-Propyl Chloride 33%
Ethyl Chloride ..	1, 1-Dichlorethane 87% 1, 2-Dichlorethan 13%
n-Propyl Chloride ..	1, 1-Dichloro 41% 1, 2-Dichloro 26%

For nucleophilic (anionoid) reactions, we have a number of examples. Except for the difference that has to be expected in changing from the first to the second member, the contribution of the resonance energy in any single series of reactions involving the same bond can be expected to be the same and the Activation Energy for the reaction remains constant. Differences in the rate constant arise primarily from differences in the frequency factor. This is seen from Table III.

TABLE III. *Activation Energies in Homologous Series*

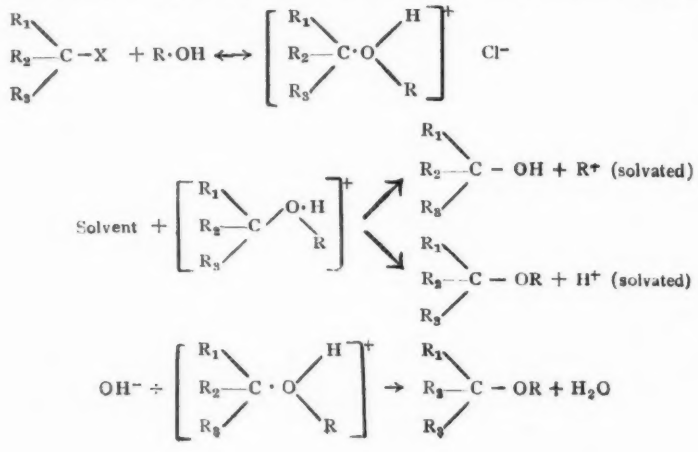
R	$RI+PhCH_2ONa$ ( )	Saponification of Alkyl Acetates ( )	$R Cl+I'$ ( )
CH_3 ..	20,570	..	..
C_2H_5 ..	21,860	11,210	..
n C_3H_7 ..	21,730	11,320	18,610
n C_4H_9 ..	21,560	11,370	19,610
n C_5H_{11} ..	..	..	18,370
n C_6H_{13} ..	..	..	18,620
n C_7H_{15} ..	21,510	..	18,990
$C_{16}H_{33}$ ..	21,090	..	19,040

Since the transition state represents here a resonance hybrid structure involving the reactants and the products in which the contribution by the product must necessarily be more than the initial reactants, one should expect by alteration of the conditions for a reversal of the position. This is well illustrated by the reaction between methyl halides and the halide ion, since the bond energies do not differ by large amounts for a change in either direction. Taking bromides and iodides for the reaction $Me\text{-}X + Y^- \rightleftharpoons MeY + X^-$, if solvent influences are absent, the difference in activation energy for the forward and reverse reactions should remain the same as is observed. Considering the difference in sizes, however, frequency factors may not be expected to be the same and decide the position of equilibrium. In the study of these reactions in hydroxylic solvents, there is the invariable complication of solvolysis as has been clearly demonstrated by Hughes and Ingold (15). We have to fit in their well-established mechanism of this process with our present picture. A solvated complex is a necessary first stage which does not actually enter into the kinetic order equation and alternative representations are possible for this. Amis (1) represents the governing steps as follows:

$$(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3CCl \cdot H_2O$$

$$(CH_3)_3CCl \cdot H_2O + OH^- \rightarrow (CH_3)_3C \cdot OH + H_2O + Cl^-$$

Hughes and Ingold (*loc. cit.*) have considered this and rule out a monohydrate as a possible step and feel that a larger number of water molecules must contribute to the energising of the C-X bond. An approximate calculation from the dimensions of the molecules involved shows that this number even for a close-packed ' atmosphere ' round the dipole may not exceed four, of which only one participates in the reaction giving the following picture:



The formation of alcohols and ethers by solvolysis involve only a single mechanism and the change in pH during the hydrolysis of tertiary butyl chloride is readily understandable.

Our justification for the view that in the attack by the solvent, it is the carbon of the C-Hal. bond that is involved is the hypothesis of Bernal and Fowler (8) that halide ions are not hydrated. Based on this, Stokes and Robinson (25) find that in univalent cations the hydration number is in the order $I > Br > Cl$ and the heavier univalent cations are associated with only one or two water molecules. A consequence of the suggested mechanism is that in solvolysis involving the C-Hal. bond, the principal difference in activation energies will be related to the bond energy so that tertiary halides are more easily hydrolysed than secondary which in turn are more easily hydrolysed than primary. The much larger difference in the rate is traceable to differences in the frequency factor which will be considered later. Further, among tertiary halides, the activation energy should remain essentially the same. The small range (about 10%) observed by Hinshelwood (14) can arise partly from hyperconjugation and partly from the differences in solvation with increasing size of the cation.

The reaction mechanism in the case of olefin additions is still far from clear but, where one can presume a similarity in the mechanism, a close correlation between the characteristic vibration frequency and the activation energy for the reaction has been noticed (5).

Aromatic compounds provide us with a variety of reactions of all the three types and a consideration of Arrhenius parameters is particularly needed where such reactions have been used to indicate fixation of bonds. There is, however, a paucity of rate measurements and generalisations have to be based often on the relative yields of products with substituents in the different positions. Further in most cases while we have the yields of the major product, information on the remaining product or products is rarely available. In spite of these limitations, it is possible to study the necessity or otherwise of the postulate of bond-fixation. For the three types of reagents, the electronic requirements necessarily vary.

We have only one clear case of a simple benzene derivative being substituted by a free radical mechanism (Loebl, Stein and Weiss 27) and as may be expected, all three positions are substituted and it is interesting to note that nitrobenzene gives the largest proportion of *p*-nitrophenol and the smallest proportion of the meta compound. This is in conformity with the picture of the transition state given by Wheland (28). A proper assessment, however, requires more information.

In dealing with the problem of bond fixation, the reactions of interest are essentially ionic reactions or those involving polarised molecules. An analysis of observations with simpler molecules clearly enables us to form a picture of the more complex structures in which the Mills-Nixon Effect has been reported. Ingold and co-workers (17) have studied the kinetics of nitrations and have also provided us with a full information on the relative amounts of the substitution products but we do not have any values of activation energies. As an approximation, no large error may be introduced by assuming the same frequency factor for the different substituted benzenes. This will not also vitiate comparisons among the positions of the same compound as the relative values will be the same as any error is in a factor which affects all the positions equally. While absolute values are not feasible, using the procedure which has been found useful in the case of bromine addition to olefines (5), the change in activation energy for the different postions taking Benzene as the standard can be computed (Table IV).

TABLE IV. *Difference in Activation Energies for Different Positions*

(A minus sign before number indicates that E is less than benzene by the quantity mentioned.)

Substance	Excess of E over that of benzene in kilocalories		
	Ortho	Meta	Para
Toluene ..	−3·85	−1·10	−4·0
Ethyl Benzoate ..	6·0	6·5	7·0
Chlorobenzene ..	3·5	19·8	2·0
Bromobenzene ..	3·5	19·8	2·3

Applying the same principle to a disubstituted compound:

taking the position 4 which is the one of highest yield as standard, we find the ramaining positions requiring a higher activation energy in the order

position 5: 2·95K.cals.
position 3: 3·05 K.cals.
position 6: 5·2 K.cals.

The differences can arise essentially from variations in the structures that contribute to the resonance energy of the transition state. In all the examples, there is no question of bond fixation involved. Mention should also be made here to Eyring's studies (11) which have shown that the charges in the different positions show corresponding differences.

Halogenaiton of halogenobenzenes has not provided us with kinetics data but we have the yields of the different substitution products. Following Eyring's method, Wibaut's (29) observations were found by the author (3) to lead to a value for the dipole moment of these compounds at higher temperatures above about 450° C. which was the same as for aliphatic analogues. Judging from the relative proportions of the isomers, one has to infer a temperature variation of activation energies which makes the meta position more reactive at the higher temperatures.

Hinshelwood and co-workers (13) have studied the sulphonation of several benzene derivatives but we are not able to use them for our present purpose as we do not have the information of the relative amounts of the substitution in the different positions.

The information we have gathered in the preceding paragraphs is enough for a fuller analysis of the evidences adduced for bond fixation on the basis of reactivity at specified positions which were only briefly considered in the earlier communication (6).

The reaction that has been most extensively used for the postulate of bond fixation is the coupling of diazo compounds and this also happens to be the most consistent of the reactions. We shall, therefore, examine this in some detail. The coupling reagent is one of the following depending on hydrogen-ion concentration of the reacting system:

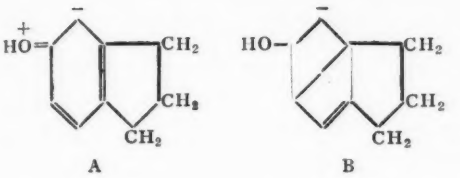
$$[Ar - N = N - O]^- M \text{ or } [Ar - N \equiv N]^+ \chi^- \quad (Ar = \text{Aryl})$$

$$M = \text{Metal}$$

A free radical mechanism has been suggested (22) but an ionic mechanism appears to be more consistent with all observed facts. The transition state for the coupling reaction may be represented as follows:

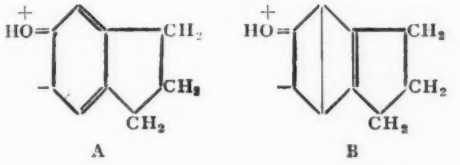
While this is the general picture, the activation energy for coupling in the different positions will depend on the contribution of excited structures which tend to have the desired charge in the particular positions. Further for an ion dipole reaction, the potential function has been shown by Amis and

Jaffe (2) to involve the external moment of the molecule. The vectorial property of dipole moments makes the structure with the charge in the para position the most favoured for reaction. Hence we find coupling generally in the para position with ortho positions following. The meta positions involve a minimum contribution by excited structures with the result that activation energy for these positions will be a maximum. It has been noticed in the earlier part of this note that small differences in the activation energy cause considerable difference in the relative amount of the substitution product and the absence of coupling in the meta position is therefore quite understandable. The observations of Auwers (7) as well as those of Friedlander (12) on "steric hindrance" in coupling reactions are quite consistent with the above picture. Differences among substituents and the same substituents in different positions alter the activation energy by the differences in the contributions of the excited structures to the resonance hybrid of the transition state or alter the dipole moment or influence both these. It is necessary to mention here about instances where coupling is accompanied by replacement of an alkyl radical and the coupling reactions of certain hydrocarbons. A lowering of the activation energy for the coupling reaction can be brought about either by the activation of the position of coupling or by the presence in the diazo component of groups which stabilise a diazonium cation. Meyer's (21) observations on the coupling of diazotised picramide with poly alkyl benzenes indicates that for the transition state to change over to the products over and above the contribution of excited structures in providing the correct charge distribution at the coupling point, the minimum dipole moment caused by the presence of an alkyl group para to the coupling position appears to be a further necessity. In durene this condition is not fulfilled and coupling does not take place. Where replacements occur, one has to presume contribution of quinonoid structures to the transition state in which the group replaced can split of as a cation. To complete the picture, one may refer to the calculations of Pullman (24) which clearly show an excess negative charge in ortho and para positions of phenol. With polynuclear systems, it will be necessary to consider the contributions of structures involving phantom orbits to the resonance energy in the computations of activation energy for the reaction. Sufficient has been said to take up the view that there is no need to consider that there is any bond fixation to explain the observations regarding the position coupling. Taking the special case of 5-hydroxy hydrindene which gave rise to this concept, the structures which might contribute to the transition state for couplong in the four and the six position are as follows:

(I) 

A B

Structures with positive charge on carbon atoms

(II) 

A B C

Structures with positive charge on carbon atom

C

The contribution by structures with a charge on the carbon atom involving second excited structures is not likely to be appreciable in either case and only A and B need be taken into account. Longuet-Higgins and Coulson have shown (19) that activation energy involved in forming I-A will be larger than that in forming II-A. The formation of structure I-B requires a change from a trigonal to a tetrahedral carbon while in II-B the carbon atoms common to the two rings are not altered and as such the formation of the latter structure can also be expected to involve a lower activation energy. The net result will be that for all electrophilic or cationiod reagents, the favoured seat of reaction has to be 6 and not 4 without any need to postulate bond fixation.

The Frequency Factor

In our analysis so far our attention has been confined to only one of the parameters of the reaction rate equation. We shall now briefly consider the frequency factor. We shall further limit our attention only to "slow" reactions as the commonest reactions of organic compounds belong to this category. It was observed by the author (4) that the experimental value of the factor was essentially the same as the calculated value if a correction term is introduced. This correction term is reckoned as the ratio of the square of the bond length of the bond involved in the reaction to the square of the molecular diameter (4). Where a reaction consists of more than one stage, one may expect this factor to involve the product of the probability of encounter in the right phase in each step. This has been done in the case of both acid and alkaline hydrolysis of esters of substituted benzoic acid and the same correspondence has been observed. This is being communicated separately (20). An example with the mechanism used for the calculations, however, may not be without interest and is given below:

TABLE V

Compound	Mechanism	PZ (Calc.)	PZ (Exp.)
Ethyl Butyrate ..	Acid hydrolysis (Ingold)	$1 \cdot 01 \times 10^{8}$	$1 \cdot 29 \times 10^{7}$ (10)
Ethyl Benzoate ..	,,	$7 \cdot 66 \times 10^{7}$	$6 \cdot 92 \times 10^{7}$ (10)
Ethyl Toluate ..	,,	$7 \cdot 33 \times 10^{7}$	$7 \cdot 58 \times 10^{7}$ (10)
Ethyl Benzoate ..	Alkaline hydrolysis (10)	$7 \cdot 38 \times 10^{7}$	$4 \cdot 68 \times 10^{7}$ (19)

The agreement between the last two columns is adequate to warrant the conclusion that where a reaction takes place involving several steps, the ' probability ' of a reaction going to completion depends on the reaction path following a narrow path in each of the stages. One has to reckon with a transition state for each stage of the reaction, however small the interval of time and the smallness of the P factor is an indication of the rigid phase relationship of encounters necessary for completion of change. Similar calculations can be attempted for other reactions in which the mechanism is established and the Menschutkin reaction is considered in a separate communication.

While quantitative data are inadequate for test, it is not difficult to see that in the coupling reactions of diazo compounds, normally only one diazonium compound couples and that the entrance of a second diazo group is relatively slow and the formation of the bis-azo compounds often needs changes in the experimental conditions. The formation of the monoazo derivative naturally results in the formation of a larger molecule for the second encounter but the advantage of a larger diameter is more than offset by a reduction of the chances of encounter at the right phase and the ratio r^2_{C-X}/molecular diameter^2 which approximately has been taken in some of our earlier calculations as giving the order of magnitude of the P factor is considerably smaller for the second coupling. Hence the reduced rate observed. Similarly, part of the observed rate variation in rate of esterification of primary, secondary and tertiary alcohols can be attributed to this.

We are still far from a complete picture of reaction rates but it is nonetheless clear that the use of reactions in fixing the structure of complex organic compounds has its limitations and a consideration of the Arrhenius parameters shows up these limitations. The conventional formulæ of organic chemistry is more a piece of convenient symbolism than a complete picture of the force binding the different atoms.

Summary

Experimental data on different reactions commonly used in the study of organic compounds have been studied and the parameters of the reaction rate equation considered in relation to mechanism and the structure of the compounds. The limitations of these reactions and the relation of reactivity to the Arrhenius parametrs is also brought out.

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320-50 Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao, Superintendent
and Published by The Indian Academy of Sciences, Bangalore

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